DEGRADATION OF WATERBORNE CONTAMINANTS BY OZONE AND HYDROGEN PEROXIDE

by

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STATEMENT OF DISSERTATION APPROVAL

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ABSTRACT

Worldwide, anthropogenic contaminants emerge and enter into aquatic systems; their ubiquity in aquatic systems poses serious threats to both human health and ecological systems. As the demand for water continues to grow with population, treatment of wastewater and remediation of polluted aquatic systems are of critical concern. Ozonation and advanced oxidation processes (AOPs) are promising methods for removal of numerous waterborne contaminants. In this thesis, three groups of waterborne organic contaminants have been studied for degradation by uses of ozone and ozone in combination with hydrogen peroxide. Specifically, the study compounds are methyl *tertiary*-butyl ether (MTBE), six endocrine disruptor compounds (EDCs) and pharmaceutical and personal care products (PPCPs) chemicals that include dibutyl phthalate (DBP), diethyl phthalate (DEP), dimethyl phthalate (DMP), di(2-ethylhexyl) phthalate (DEHP), bisphenol A (BPA), triclosan (TCS), and two naphthenic acids (NAs) including Cyclohexaneacetic acid and Cyclohexanebutyric acid. This study has also examined a pressure assisted ozonation (PAO) method that employs ozone microbubbles generated by repetitive compression-decompression cycles to treat the study compounds. Degradation has been investigated under different conditions. The results indicate that ozonation is very effective in removing these contaminants, and that PAO increases treatment efficiency by 10 to 40% for different chemicals. MTBE degradation by 90% was achieved in 36 min from an initial concentration of 12 mg/L. TCS and BPA

disappeared completely within minutes of PAO treatment from an initial of 9 mg/L. The removals of four phthalate esters were between 45%~98% in 24 min from initial concentrations of 6.9 – 8.6 mg/L. For NAs, a high concentration of ozone (e.g., 15 mg/L) along with a proper dose of H_2O_2 (e.g., H_2O_2/O_3 mole ratio 1/1) completely removed the study NAs from an initial concentration of 17 mg/L in 10 min. Varying treatment parameters significantly influenced treatment outcomes: e.g., addition of H_2O_2 increased removal percentage of different chemicals by 10 to 30%; increasing compression cycles improved removal of target compounds to a certain degree. Aqueous O_3 concentration was an important factor, with increased removal at higher O_3 concentration. The pH range between 7 and 10 was more suitable treatment condition than pH 3 for degradation of the target compounds. Initial target compound concentration, however, did not influence removal rate significantly.

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CHAPTER 1

INTRODUCTION

1.1 Waterborne contaminants

Anthropogenic contaminants have become ubiquitously present in aquatic systems including surface waters and groundwater. Among the pollutants are pesticides, herbicides, fertilizers, petroleum products and byproducts, industrial chemicals, heavy metals, and pharmaceutical compounds [1]. By 2004, nearly 23 million organic and inorganic substances had been indexed by the Chemical Abstracts Service of American Chemical Society [2]. Worldwide, new contaminants emerge yearly that find their ways into the aquatic systems via manufacturing emissions, accidental spills, landfills, waste ponds overflow, septic tanks leakage, land application, agricultural and mining waste permeation, and others [3]. These waterborne contaminants are present in the waters at a wide concentration range, occasionally reaching hundreds of mg/L. At times, they have shown clear adverse effects on both human health and the ecological systems.

For example, ethylene dibromide (EDB), a gasoline additive among the most commonly detected contaminants in groundwater, is classified as a probable human carcinogen and is highly persistent in water. For use as a solvent stabilizer, 1,4-Dioxane is a widespread contaminant in groundwater and a probable human carcinogen [4]. Herbicide sulfonylurea (SU) is toxic to aquatic plants such as algae and duckweed at

several micrograms per liter [5]. Brominated flame retardants such as polybrominated diphenyl ethers (PBDE) are found to suppress the growth of algae, cause liver disease, and restrain fetus development in mammals [6]. Many compounds such as pesticides, pharmaceuticals, hormones, petroleum products, plasticizers, detergents show endocrine disrupting properties that alter proper functioning of endocrine systems in organisms or human being, resulting in psychomotor development delay, endometriosis, reproductive abnormalities, infertility, and certain cancers [7].

As the demand for water continues to grow with population, water supplies in many areas necessitate recycle and reuse. Consequently, the treatment of wastewater and remediation of polluted surface and subsurface waters are of critical concern. Ozonation and advanced oxidation processes (AOPs) are promising techniques for removal of many waterborne contaminants. In this thesis, three groups of waterborne contaminants were chosen for evaluation of treatment by ozone and by ozone with hydrogen peroxide. They are methyl *tertiary*-butyl ether (MTBE), six endocrine disruptor compounds (EDCs) and pharmaceutical and personal care products (PPCPs) compounds that include dibutyl phthalate (DBP), diethyl phthalate (DEP), dimethyl phthalate (DMP), di(2-ethylhexyl) phthalate (DEHP), bisphenol A (BPA), triclosan (TCS), and two naphthenic acids (NAs) including Cyclohexaneacetic acid and Cyclohexanebutyric acid. The study compounds are all emerging contaminants or priority pollutants, released into the aquatic environments and subject to migration with the waters. They are toxic to aquatic lives at low concentrations and pose serious threats to human health when present in drinking water. The compounds are typically resistant to biodegradation and only partially removed in wastewater treatment, thus demanding further treatment.

1.2 Methyl *tertiary*-butyl ether (MTBE)

Methyl *tertiary*-butyl ether (MTBE) is a volatile organic compound derived from natural gas. It has been used as an octane enhancer in gasoline in the U.S. to increase the efficiency of combustion and decrease the emission of carbon monoxide for nearly three decades [8]. It is a primary constituent in reformulated gasoline, accounting for approximately 10-15% by weight of the reformulated fuels [9]. Because of its physical and chemical characteristics and fate in the environment, MTBE has caused significant concern over environmental health. It has a high solubility in aqueous phase and low affinity for sorption to soil. It migrates faster and farther in groundwater than other gasoline components, making it more likely to contaminate public water systems and private drinking water wells [10]. As a result, MTBE was detected in groundwater throughout the country. According to studies by the U.S. Environmental Protection Agency (EPA), low levels of MTBE renders water undrinkable by its offensive taste, odor, and carcinogenicity at high doses [11]. MTBE is not amenable to conventional treatments. It has high solubility in water that limits adsorption onto activated carbon, low Henry's law constant that limits the effectiveness of air-stripping, and a robust chemical structure that resists biodegradation [12]. MTBE is a threat to underground water supplies. California banned the use of MTBE in 2002. Several states and air quality non attainment areas are trying to get out of the federal reformulated gasoline and oxy-fuel programs, mostly to help avoid MTBE [13]. In 2005, driven by state bans due to water contamination concerns, a number of petroleum companies announced the removal of MTBE from gasoline in 2006 and the industry attempted to move away from MTBE by 2006 [14].

1.3 EDCs and PPCPs

Endocrine disruptor compounds (EDCs) and pharmaceutical and personal care products (PPCPs) were emerging contaminants found in the various waters and became the focus of environmental research in recent years [15-16].

EDCs were defined by the American Water Works Association (AWWA) as chemicals that interfered with the normal function of the endocrine system [17]. They had the potential of causing adverse health effects on humans and wildlife [18], including stillbirth, cancer, reproductive abnormality, decrease in male birth in human, neurological development in children, reproductive ailments and reduced fertility in fish and mollusk, and antiandrogen effects on mammals [7].

According to EPA, PPCPs are referred to as "any product used by individuals for personal health or cosmetic reasons or used by agribusiness to enhance growth or health of livestock" comprising a diverse collection of thousands of chemicals [19]. PPCPs are often persistent in the environment and some have recognized endocrine disruption functions [20], which overlap with the effects of EDCs. Other adverse effects of PPCPs on ecosystem or human health include reduction in algal genus diversity [21], potential carcinogenicity, developmental problems, and systemic damages [22].

EDCs and PPCPs are ubiquitous in the waters (streams, drinking waters, seawater, groundwater, wastewaters) at very low concentrations ranging from ng/L to μg/L [23-26]. They entered the waterways mainly by direct discharge, sewage effluent, and agricultural runoff [7], They often survived the conventional wastewater treatment processes, eventually entering water resources or water supplies [27]. EDCs and PPCPs often have adverse impacts on both human and natural organisms at low concentrations, thus it

would be desirable to treat these chemicals at an advanced stage after conventional wastewater treatment processes.

There are many methods for the removal of EDCs and PPCPs from waters such as membranes filtration process, adsorption, and oxidation. A pilot treatment study of EDCs and PPCPs found that following the ferric sulfate coagulation, vertical sedimentation, and rapid sand filtration, PPCPs (including acebutolol, metoprolol, sotalol, ibuprofen, carbamazepine, naproxen, etz.) were removed by an average of 13%; ozonation was more efficient, removing PPCPs to below limit of quantification value, with exceptions for naproxen at 75% removal and ciprofloxacin at 16% removal [28].

While membrane bioreactors (MBR) removed estriol, androstenedione, acetaminophen, ibuprofen, and caffeine by >93%, MBR has limited removal ability for hydrocodone, trimethoprim, diclofenac, and carbamazepine. while membrane filtration processes such as reverse osmosis (RO) and nanofiltration (NF) showed effective removal (>95%) for all studied compounds [29].

In a bench scale drinking water treatment study, chlorine oxidation was found to eliminate some EDCs and PPCPs such as acetaminophen, estradiol, estriol, estrone, ethynylestradiol, oxybenzone, and triclosan very effectively (>95% in 24 h), yet some other compounds were resistant to chlorination, such as *N*, *N*-diethyl-*m*-toluamide, meprobamate, tri(2-chloroethyl) phosphate, and heptachlor epoxide (<30%).

Powder Activated Carbon (PAC) eliminated EDCs and PPCPs by 14% to 98% depending on the PAC types and dosages, target chemical properties, and contact time [30].

1.4 Naphthenic Acids (NAs)

Naphthenic acids (NAs) are carboxylic acids that include one or more saturated ring structures and are predominately monocarboxylic acids [31]. Nonvolatile and chemically stable, they are natural components of crude oil at varied concentrations depending on the source of oil [32]. NAs account for up to 4% by weight in crude oil sands [33]. In extraction of bitumen from oil sands with caustic hot water, NAs are released to tailings ponds, resulting in 40–120 mg/L of NAs in affected water [34]. NAs in tailing ponds can enter natural water systems through leaking or erosion of riverbank oil deposits [35]. NAs are also found in wastewater streams from petroleum refining [36]. NAs are toxic to many aquatic organisms, including microorganisms, crustaceans, and fish [37]. Rogers et al. studied mammalian toxicity of NAs and identified their cardiovascular and hepatic effects on Wistar rates at levels of 300 mg/Kg [38]. Frank et al. found greater toxicity of NAs of lower molecular weight (median value 223 Dalton) [37]. Holowenko et al. found NAs with carbon number <21 contributed to most of the NAs toxicity [34]. Chun et al. also suggested the toxic potency of NAs as being related to their structure, with reduced toxicity associated with more rings [39].

To eliminate the toxicity of NAs and prevent its damage to the ecosystem, NAs need to be removed from tailing pond and petroleum refining wastewaters. Biological treatment of naphthenic acids has been studied. Under aerobic condition, NAs concentrations were reduced from about 100 to less than 10 mg/L in 10 days [40]. Other treatments included ultrafiltration [41], sorption by polymeric materials [42] and ozonation [43]. Of these processes, ozonation appeared to be a promising method

demonstrating over 95% removal of NAs (from an initial concentration of 60 mg/L) from oil sands process water within 130 min [43].

1.5 Ozonation, AOPs, and their application in water treatment

Ozone (O_3) is an allotropic modification of oxygen [44]. It is a highly oxidizing gas with a high standard redox potential; it readily decomposes and therefore must be produced at the point of use. O_3 reacts with organic compounds directly in the form of $M+O_3$, which has a slow reaction rate constant ($1.0\sim10^3$ $M^{-1}S^{-1}$). O_3 also reacts with organics indirectly in complex radical pathways with faster rate constants. Initiation and chain reactions of indirect reaction generally involve [45]:

$$O_3 + OH^- \rightarrow O_2^- \bullet + HO_2\bullet \quad (1.1)$$

$$HO_2\bullet \longleftrightarrow O_2^- \bullet + H^+ \quad (1.2)$$

$$O_3 + O_2^- \bullet \rightarrow O_3^- \bullet + O_2 \quad (1.3)$$

$$HO_3\bullet \longleftrightarrow O_3^- \bullet + H^+ \quad (1.4)$$

$$HO_3\bullet \rightarrow \bullet OH + O_2 \quad (1.5)$$

$$\bullet OH + O_3 \rightarrow HO_4\bullet \quad (1.6)$$

$$HO_4\bullet \rightarrow O_2 + HO_2\bullet \quad (1.7)$$

In an O_3/H_2O_2 system, H_2O_2 is used in conjunction with O_3 to enhance the formation of hydroxyl radicals (·OH) [46]. When O_3 is added to water, it participates in a complex chain of reactions that result in the formation of radicals such as ·OH and the

superoxide radicals ($O_2\cdot$), which are more powerful oxidants than O_3 and will further catalyze the depletion of molecular O_3. H_2O_2 can be combined with O_3 to enhance the formation of ·OH in aqueous solution, it partially dissociates into the hydroperoxide ion (HO_2^-) in water, H_2O_2 reacts slowly with O_3, whereas HO_2^- can react rapidly with O_3 to form ·OH [47] . These processes are as shown in Equation (1.8) to (1.12).

$$O_3 + H_2O \longleftrightarrow O_2 + 2\ \bullet OH \quad (1.8)$$

$$O_3 + \bullet OH \longleftrightarrow HO_2^- + O_2 \quad (1.9)$$

$$H_2O_2 + H_2O \longleftrightarrow HO_2^- + H_3O^+ \quad (1.10)$$

$$O_3 + HO_2^- \longleftrightarrow \bullet OH + O_2 + O_2^- \quad (1.11)$$

$$O_3 + O_2^-\bullet \longleftrightarrow O_3^-\bullet + O_2 \quad (1.12)$$

Ozonation has been applied in water treatment for nearly a century. It has multiple applications in both drinking water and wastewater treatments, its main uses include:

- Disinfection and biocide for algae;
- Oxidation of inorganic pollutants such as for iron and manganese;
- Oxidation of organic pollutants with taste, odor, and aesthetic issues such as for phenolic compounds and pesticides;
- Destruction of trihalomethane and reduction of halide formation;
- Improvement of coagulation [48].

The treatment of drinking water and wastewater with ozone is still increasing in the U.S. and worldwide. Water treatment plants are increasingly equipped with ozonation process. Ozone applications are advancing in control of disinfection byproducts (mostly

chlorination byproducts) and in biological stabilization (control of microbiological growth) [48].

Advanced oxidation processes (AOPs) are based on the formation of hydroxyl radicals and their fast destructive reactions with water pollutants [49]. AOPs make use of different reactant systems, such as with H_2O_2/Fe^{2+} (Fenton), $H_2O_2/Fe^{2+}(Fe^{3+})$/UV (photo Fenton), Mn^{2+}/Oxalic acid/Ozone, $TiO_2/hv/O_2$ (Photocatalysis), O_3/H_2O_2, O_3/UV, and H_2O_2/UV [50]. O_3/H_2O_2 reactant system was among the most frequently used AOPs.

AOPs represent an attractive technique for destroying MTBE in water [51]. AOPs exploit the principle that MTBE can be chemically or physically oxidized to CO_2 and H_2O. The oxidants include hydrogen peroxide, ultraviolet light, and ozone. Past research using AOPs to treat MTBE-contaminated water achieved 99% removal. Marco et al. combined the uses of photocatalysis, H_2O_2 photolysis, and sonolysis to degrade MTBE and concluded highest degradation effectiveness with hydrogen peroxide under photolysis at 254 nm, which achieved complete MTBE degradation in 20 min [52]. Fenton was very effective in oxidizing MTBE; according to Siedlecka et al., this reaction was inhibited by chloride. In absence of chloride ions, MTBE was removed by 97% in 90 min, while in the presence of 0.05–0.2M of chloride MTBE was removed by 85–87% [53]. As advances in AOPs are made, their use for MTBE degradation may grow and understanding of AOPs will be improved [54]. Among the AOPs, O_3/H_2O_2 process appears to be most promising, with results showing their greater effectiveness than UV/H_2O_2 in remediation of MTBE-contaminated groundwater [55].

The treatments of pharmaceutical metronidazole by Fenton and photo Fenton processes were compared. The results indicated that pH 3.5 favored high ferrous ion

concentration that led to increased removal of metronidazole, while photo Fenton was more efficient than Fenton achieving 95% and 75% removal in 5 min, respectively [56].

Studies have shown that UV/H_2O_2 processes were capable of destroying many EDCs and PPCPs effectively. Ethinyl estradiol and estradiol could be degraded by more than 90% with medium pressure UV lamp dosed with 15 ppm of H_2O_2 [57]. In another study, UV/H_2O_2 reduced the toxicity of PPCPs and completely removed six selected pharmaceuticals in only minutes [58].

O_3 and O_3/H_2O_2 processes were applied for removal of EDCs and PPCPs. An ozone dose of 2 mg/L resulted in 40 – 70% in transformation of 0.5 μM of ibuprofen in 10 min; when 0.7 mg/L of H_2O_2 was added, the transformation increased to 78 – 90% [59]. In a study using O_3 at 13 g/h for pesticides, 16 mg/L of isoproturon was completely removed in 30 min, while 20 mg/L of alachlor was completely removed in 270 min [60].

1.6 Pressure-assisted ozonation - PAO

Recently, a unique pressure-assisted ozonation (PAO) technique involving expanding microbubbles was developed that resulted in degradation of recalcitrant contaminants with effectiveness not possible before with conventional ozonation [61]. Briefly, during PAO treatment, an ozone/air mixture is compressed by an air compressor and introduced into a reactor with a closed headspace above the contaminated water being treated. The compression is carried to a prescribed elevated pressure (e.g., 100 psi) in the headspace, thus oversaturating the water with air and ozone beyond what is normally dissolved at ambient pressure. When the target pressure (e.g., 100 psi) in the reactor is reached, ozone pressurization ceases and the pressure is released by venting at a

controlled rate, facilitating the generation of gaseous, O_3-rich microbubbles within the water being treated. The time for compression depends on the headspace, ozone/air mixture flow rate, and the power of the air compressor - usually within one minute; the time for decompression varied with gas venting rate but typically in seconds. The compression-decompression cycle is rapidly repeated a number of times as necessary for sufficient degradation of contaminants. Other PAO treatment parameters such as pressure, reactor headspace, ozone flow rate, ozone concentration, addition of other oxidants such as hydrogen peroxide are varied for different contaminants in the water.

The application of PAO is used to accelerate ozonation treatment of a wide range of organic contaminants and has been used to treat soil and sediment slurries contaminated by recalcitrant organics [62]. During PAO treatment of slurry, when the slurry was pressurized, the sediment particles were fractured under successive pressure cycles, allowing increased exposure of contaminants to ozone and improved removal of contaminants.

PAO can be applied in on-site treatment of produced water, wastewater in tailing ponds of oil sand extraction, landfill leachate, or before or after other processes such as biological or membrane processes. A recent study showed effective removal of dispersed and dissolved oil and oil sheen from produced water using combined PAO and sand filtration (SF) [63]; PAO was found to be more effective than conventional bubbling ozonation in converting nonpolar hydrocarbons to hydrophilic compounds that are more amenable to removal by SF.

Figure 1.1 illustrates how PAO works.

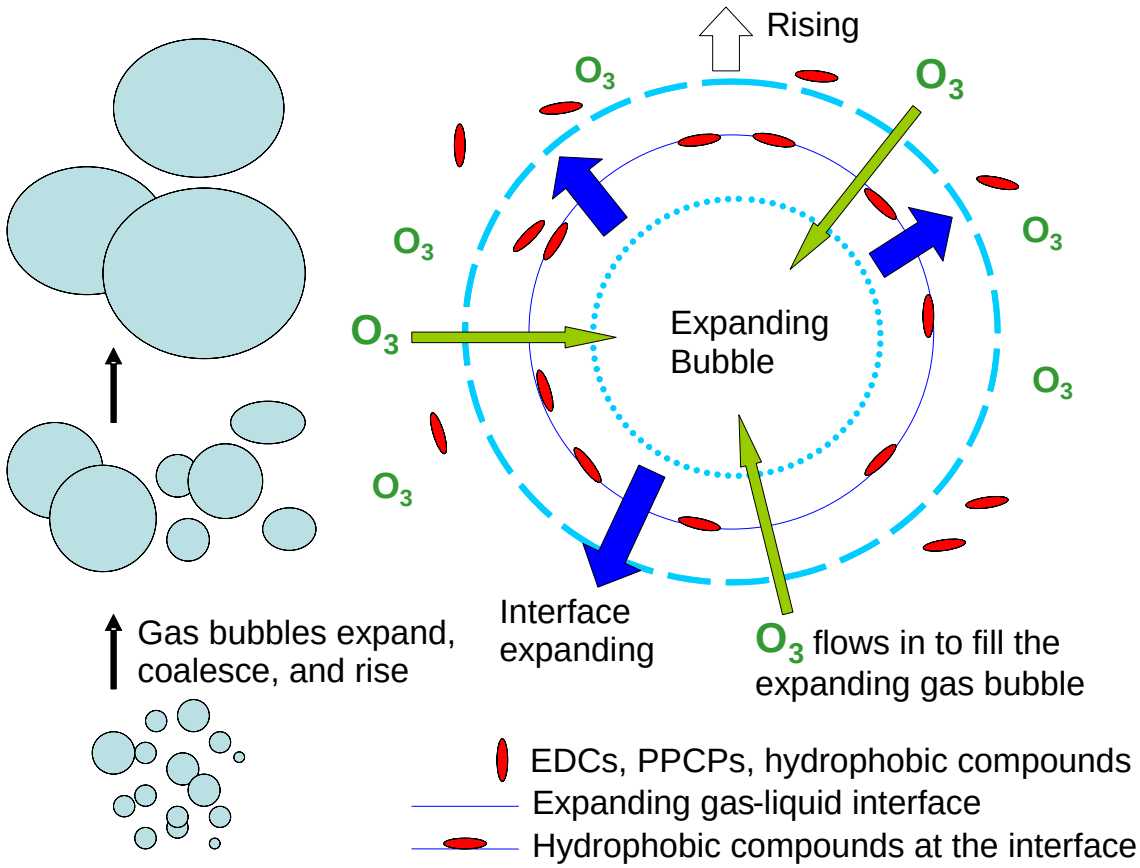

Figure 1.1. Heightened treatment of contaminants in water by expanding microbubbles

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CHAPTER 2

RESEARCH OBJECTIVE AND HYPOTHESES

2.1 Objective

The objective of this work was to study the treatment by ozonation and modified methods of 9 waterborne contaminants, including Methyl *tertiary*-butyl ether (MTBE), six selected EDCs and PPCPs chemicals that include dibutyl phthalate (DBP), diethyl phthalate (DEP), dimethyl phthalate (DMP), di(2-ethylhexyl) phthalate (DEHP), bisphenol A (BPA), triclosan (TCS), and two naphthenic acids (NAs) Cyclohexaneacetic acid and Cyclohexanebutyric acid that are commercially available. The treatment methods include:

1. Conventional bubbling ozonation (O_3 only);
2. Conventional advanced oxidation process of ozonation with hydrogen peroxide (O_3/H_2O_2);
3. Ozonation in pressure cycles of compression and decompression – Pressure-assisted ozonation (PAO).

The selected study compounds are all organic, waterborne, and among the most commonly detected and concerned. They are products and byproducts spanning across many industries including the pharmaceutical, the chemical, and the energy sector. The

compounds often appear on various lists of concern such as priority pollutants, persistent organic pollutants, endocrine disruptor compounds, emerging contaminants, pharmaceutical and personal care products, and others. Ozonation has been well practiced for decades and used for many contaminants; however, ozone is effective to different degrees of success for these compounds and for some of them not effective at all. Thus, an important goal of this study is to establish and evaluate the treatment effectiveness with the pressure-assisted ozonation technique in comparison to conventional ozonation, determine optimal treatment conditions of PAO for different target contaminants, and further advance the PAO technique.

2.2 Hypotheses

The ample interfacial zone surrounding the expanding microbubbles attracts and concentrates minute concentrations of target compounds at the interface, resulting in heightened contact between the contaminants with O_3 at the gas bubble interface that leads accelerated degradation. This makes effective treatment possible that would otherwise be difficult because of the typically trace concentrations of the contaminants. PAO facilitates improved treatment according to:

(1) “Sweeping” of contaminants: During compression the bulk of ozone gas dissolves into water, saturating under elevated pressure; during decompression the oversaturated gas exits the liquid phase by formation and growth of microbubbles throughout the liquid volume. The expanding gas-liquid interface of microbubbles acts to “sweep” the water body thoroughly and accumulate contaminants at the interface.

(2) Confluence of contaminants and O_3 at the interface: To fill the expanding gas volume of microbubbles during decompression, O_3 molecules are drawn across the interface where hydrophobic and amphiphilic contaminants (as many contaminants are) are accumulated. This results in heightened contact and reaction of O_3 with contaminants that would otherwise exist at diffuse state throughout.

CHAPTER 3

PRESSURE-ASSISTED O_3/H_2O_2 PROCESS FOR DEGRADATION OF MTBE

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PRESSURE-ASSISTED O_3/H_2O_2 PROCESS FOR DEGRADATION OF MTBE

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Key Words: Pressure, ozonation, MTBE, peroxone, microbubbles, interface

ABSTRACT

Contamination of groundwater by methyl tert-butyl ether (MTBE) has occurred frequently in the U.S. and been a significant concern because of its harmful effect on human health. Physical, chemical, and biological means have been used for MTBE removal; among them advanced oxidation processes (AOPs) are found to be viable for degradation of MTBE. We have developed in this study a new AOP technique using O_3/H_2O_2 in which ozone was cyclically introduced into a closed reactor; it was brought to an elevated pressure around 690 kPa followed by the release of pressure via rapid venting. This unique mode of contact between the treatment chemicals with MTBE has resulted in heightened degradation kinetics in both cases of O_3 alone and O_3/H_2O_2. The pressure-assisted degradation approximated linear profiles of zero-order behavior, removing 90% of MTBE from 11 mg L^{-1} in 36 min, in comparison to 27% removal with conventional O_3/H_2O_2 treatment. The O_3 utilization rate (mol MTBE removed mol^{-1} O_3 introduced), using the pressure cycles was 15 times that of the utilization rate without pressure cycles. The complete removal of MTBE from 12 μg L^{-1} was achieved sooner. Methyl acetate, acetone, and isobutene were found as intermediates, consistent with free radical pathways well reported in the literature. A conceptual model is proposed that explains the accelerated kinetics due to heightened contact between the contaminant and oxidants at the gas-liquid interface made available by microbubbles with the pressure-assisted process.

INTRODUCTION

Methyl tert-butyl ether (MTBE) has been used as a fuel additive in the U.S. for decades, accounting for 10-15% (w/w) of the reformulated fuels [1]. MTBE is a potential carcinogen; it has become a great concern when it leaked with gasoline from underground storage tanks, resulting in extensive soil and groundwater contamination [2]. While MTBE is phased out in the U.S. [3], many contaminated sites exist and will benefit from effective remedial solutions. MTBE is not amenable to conventional treatment techniques such as carbon adsorption and air stripping due to its physical and chemical properties; it is also very resistant to biodegradation [4,5].

Physicochemical and biological means have been explored for treatment of MTBE [6-9]. Advanced oxidation processes (AOPs) that involve the ·OH free radical have shown promise for degradation removal of MTBE [10-13]. AOPs for treatment of MTBE included the uses of Fenton agents [10-14], UV/H_2O_2 [15,16], photocatalytic UV/TiO_2 [17], ultrasound or ultrasound/O_3 [18-20], and O_3/H_2O_2 [21-23]. As a result, the kinetics and mechanisms of degradation of MTBE via •OH are relatively understood [19,20,22,23]. The free-radical pathways initiated by hydrogen abstraction from MTBE by •OH radical followed by molecular fragmentation in ensuing chain reactions have been reported.

In this study, we have developed a new contacting technique employing O_3/H_2O_2 in repetitive compression-decompression cycles for MTBE treatment. The goal is to accelerate the treatment kinetics and compare the effectiveness with conventional technique of bubbling dispersion of O_3. Reactions occurring at the gas-liquid interface of ample microbubbles are proposed to explain the heightened degradation kinetics.

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EXPERIMENTAL METHODS

All chemicals including MTBE (99%, Fisher Scientific), H_2O_2 (30%, EMD Chemicals), Isooctane (99.9%, Fisher Scientific) were used as purchased. Ozone was produced by an ozone generator (T-816, Polymetrics) with dried, filtered air at 100 V. Tap water (pH 7.4, alkalinity 130 mg L^{-1} as $CaCO_3$) was spiked with MTBE and used in degradation experiments. Figure 1 shows the experimental setup of MTBE treatment using O_3/H_2O_2 in rapid, successive compression-decompression cycles. Treatment experiments were conducted in a cylindrical, stainless steel reactor (13.2 L) at room temperature. In a typical run, tap water (11 L) was spiked with MTBE and dosed with H_2O_2; ozone/air mixture was then charged into the closed reactor bottom via tubing at up to 60 L min^{-1} to reach the designate headspace pressure (< 900 kPa) by means of a compressor. Mixing was provided by a magnetic stirrer at the reactor bottom. Venting of reactor pressure was achieved by opening of valve at the top. Compression to specified pressure took about 19 s and decompression via venting to ambient pressure occurred in 5 s; thus each compression-decompression cycle took 24 s to complete. Sample aliquots were taken at regular intervals, and the reaction mixtures were quenched by purging of N_2 gas through samples for 30 s prior to concentration procedures and gas chromatography-mass spectrometry (GC-MS) analysis for MTBE and intermediate contents.

Samples with MTBE over 50 μg L^{-1} were concentrated by a cold trapping method. A continual N_2 stream (100 mL min^{-1}) was passed through the sample (250 mL) in a glass container heated at 60 °C for 50 min, and the gas stream with stripped contents was passed into 2 mL of isooctane in a glass container kept at -80 °C by a mixture of dry ice and methanol. The process would concentrate MTBE by 100 times prior to analysis. Analysis was performed with a GC-MS (GC 6890N, Agilent Technologies; MSD 5973N, Agilent Technologies) installed with a capillary column (DB-5ms, 30 m × 0.25 mm × 0.25 μm, Agilent Technologies) and controlled by the MSD Productivity ChemStation software (Agilent Technologies). A sample of 0.2 μL was injected in splitless mode. The oven temperature was initially at 40 °C for 10 min and then increased to 100 °C at 10 °C min^{-1}, after 4 min at 100 °C, the temperature was increased to 250 °C at 30 °C min^{-1} and held at 250 °C for 1 min. Helium was used as the carrier gas at 30 cm s^{-1}. For quantitative analysis, masses of 41, 43, 57 and 73 were recorded in selective ion monitoring mode according to the main mass signals of MTBE. For calibration, MTBE solutions of 1-200 mg L^{-1} were used. Samples with MTBE under 50 μg L^{-1} were prepared by Standard Methods 5030 (purge & trap) [24] and the 8260 B [25]. MTBE

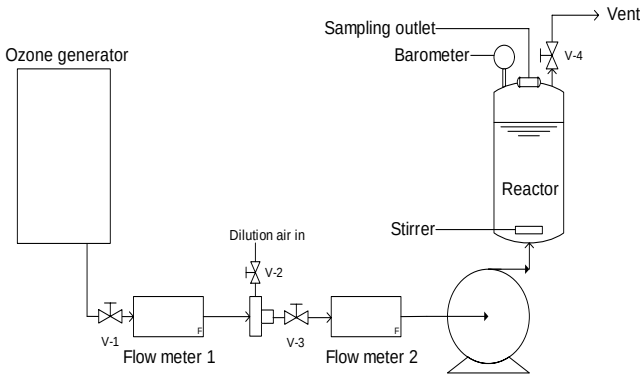

Fig. 1. Schematic diagram showing O_3/H_2O_2 treatment setup for MTBE.

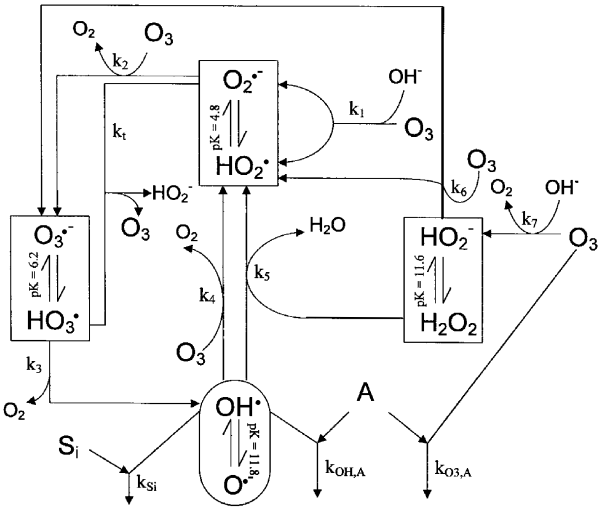

Fig. 2. Summary of free-radical chain reactions involving O_3.

solutions of 1-50 μg L^{-1} were prepared and used for calibration. Aqueous ozone concentration was measured by Indigo Colorimetric Method [26].

KINETIC MODEL AND RATE EXPRESSIONS FOR O_3/H_2O_2

Figure 2 summarizes the AOP kinetic model involving O_3 and H_2O_2 as modified from our previous work [27]. These reactions have been reported in the literature with rate constants listed in Table 1. The free radical reactions are very rapid, resulting in very low steady-state concentrations. The steady-state concentrations that can be attained by $HO_2•/O_2•^-$, $HO_3•/O_3•^-$ and $•OH/O•^-$, as well as H_2O_2/HO_2^- (regardless of whether H_2O_2 is added to the system or not) are determined by the relative kinetic rates in the formation and depletion of various free radicals. The rate expressions for these intermediates are written as:

Table 1. Rate and equilibrium constants for various reactions in the proposed AOP model. All kinetic rate constants were from references previously cited by [27]

	Reaction	Constant
Chain initiating steps	$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2$	$k_1 = 70\ M^{-1}\ s^{-1}$
	$O_3 + OH^- \rightarrow HO_2^- + O_2$	$k_7 = 48\ M^{-1}\ s^{-1}$
	$HO_2^- + O_3 \rightarrow HO_2\bullet + O_3^{\bullet-}$	$k_6 = 2.8\times10^6\ M^{-1}\ s^{-1}$
Chain propagating steps	$O_2^{\bullet-} + O_3 \rightarrow O_3^{\bullet-} + O_2$	$k_2 = 1.6\times10^9\ M^{-1}\ s^{-1}$
	$HO_3\bullet \rightarrow \bullet OH + O_2$	$k_3 = 1.1\times10^5\ s^{-1}$
	$OH + O_3 \rightarrow HO_2\bullet + O_2$	$k_4 = 1.1\times10^8\ M^{-1}\ s^{-1}$
	$OH + H_2O_2 \rightarrow HO_2\bullet + H_2O$	$k_5 = 2.7\times10^7\ M^{-1}\ s^{-1}$
Scavenging reactions	$\bullet OH + HCO_3^- \rightarrow HCO_3\bullet + OH^-$	$k_s = 1.5\times10^7\ M^{-1}\ s^{-1}$
	$OH + CO_3^{2-} \rightarrow CO_3^{\bullet-} + OH^-$	$k_{s2} = 4.2\times10^8\ M^{-1}\ s^{-1}$
	$HO_2\bullet + HCO_3^- \rightarrow HO_2^- + HCO_3$	$k_{2s} = 2\times10^6\ M^{-1}\ s^{-1}$
Terminating steps	$O_2^{\bullet-} + HO_3\bullet \rightarrow O_3 + HO_2^-$	$k_t = 10^{10}\ M^{-1}\ s^{-1}$
	$*OH\bullet + OH\bullet \rightarrow H_2O_2$	$k_{44} = 4\times10^9\ M^{-1}\ s^{-1}$
	$*HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$	$k_{22} = 5\times10^7\ M^{-1}\ s^{-1}$
	$*HO_2\bullet + OH\bullet \rightarrow H_2O + O_2$	$k_{24} = 10^{10}\ M^{-1}\ s^{-1}$
	$*HO_2\bullet + H_2O_2 \rightarrow H_2O + OH\bullet + O_2$	$k_{12} = 16\ M^{-1}\ s^{-1}$
Acid-base equilibrium	$H_2O_2 \leftrightarrow H^+ + HO_2^-$	pK = 11.6
	$HO_2\bullet \leftrightarrow H^+ + O_2^{\bullet-}$	pK = 4.8
	$HO_3\bullet \leftrightarrow H^+ + O_3^{\bullet-}$	pK = 6.2
	$\bullet OH \leftrightarrow H^+ + O^{\bullet-}$	pK = 11.8
Degradation reactions	$\bullet OH + A \rightarrow A' + OH^-$	$k_{OH,A}$
	$O_3 + A \rightarrow A''$	$k_{O3,A}$

*Reactions considered but not shown in Fig. 2; A = contaminant.

$$\frac{d[\bullet OH]_T}{dt} = k_3[HO_3\bullet]_T - k_4[\bullet OH]_T[O_3] - k_5[\bullet OH]_T[H_2O_2]_T - k_A[\bullet OH]_T[A] - k_s[\bullet OH]_T[S] \quad (1)$$

$$\frac{d[HO_3\bullet]_T}{dt} = k_2[O_3][HO_2\bullet]_T\,\alpha_1^{HO_2\bullet} + k_6[O_3][H_2O_2]_T\,\alpha_1^{H_2O_2} - k_3[HO_3\bullet]_T - k_t[HO_3\bullet]_T[HO_2\bullet]_T \quad (2)$$

$$\frac{d[HO_2\bullet]_T}{dt} = k_6[O_3][H_2O_2]_T\,\alpha_1^{H_2O_2} + 2k_1[O_3][\bullet OH] + k_4[O_3][\bullet OH]_T + k_5[\bullet OH]_T[H_2O_2]_T - k_2[O_3][HO_2\bullet]_T\,\alpha_1^{HO_2\bullet} - k_t[HO_2\bullet]_T[HO_3\bullet]_T \quad (3)$$

where A = contaminant (e.g., MTBE); S = scavenger (e.g., HCO_3^- and CO_3^{2-})

$$[\bullet OH]_T = [\bullet OH] + [O^{\bullet-}]$$

$$[HO_3\bullet]_T = [HO_3\bullet] + [O_3^{\bullet-}]$$

$$[HO_2\bullet]_T = [HO_2\bullet] + [O_2^{\bullet-}]$$

$$[H_2O_2]_T = [H_2O_2] + [HO_2^-]$$

$$\alpha_1^{HO_3} = \frac{K^{HO_3}}{([H^+] + K^{HO_3})}$$

$$\alpha_1^{HO_2} = \frac{K^{HO_2}}{([H^+] + K^{HO_2})}$$

$$\alpha_1^{H_2O_2} = \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)^{-1} \approx \frac{K_1}{[H^+]} \text{ for pH < 10.}$$

($pK_1^{H_2O_2}$ = 11.6, pK^{HO_3} = 6.2, pK^{HO_2} = 4.8, as shown in Fig. 2.)

According to the model, H_2O_2 will be formed as an intermediate and depleted during ozonation even when it is not dosed initially as governed by:

$$\frac{d[H_2O_2]_T}{dt} = k_7[O_3][OH^-] - k_6[O_3][H_2O_2]_T\,\alpha_1^{H_2O_2} - k_5[H_2O_2]_T[OH^{\cdot}]_T \quad (4)$$

The steady-state [•OH] can be determined for two different cases: 1) H_2O_2 is added as a consumable reagent added to the system, or 2) H_2O_2 is not added but formed and depleted as a reaction intermediate during ozonation.

■ When H_2O_2 is added as a reagent, steady-state •OH concentration ($[\bullet OH]_{ss}$) can be determined by solving Eqs. 1-3 simultaneously, resulting in Eq. 5:

$$[\bullet OH]_{T,ss} = \frac{2k_6[O_3][H_2O_2]_T\,K_1^{H_2O_2}[H^+]^{-1}}{k_4[O_3] + k_5[H_2O_2]_T + k_A[A] + k_S[S]} \quad (5)$$

This expression can be used to estimate steady-state •OH concentration based on instantaneous concentrations of H^+, O_3, H_2O_2, scavenger and contaminant.

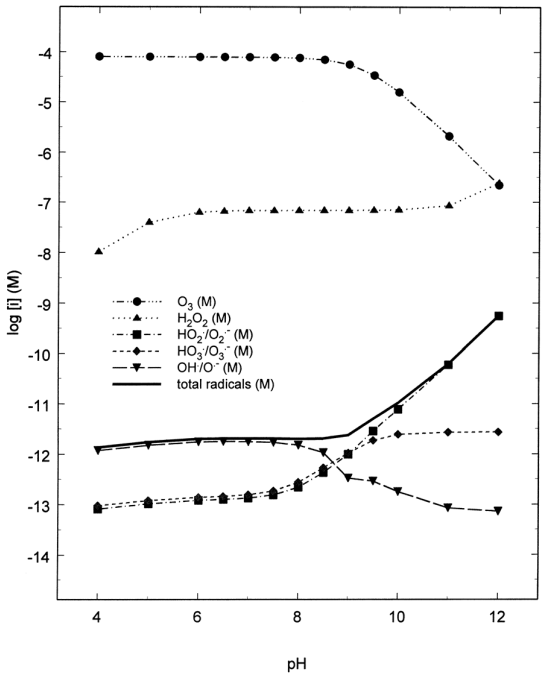

Fig. 3. Computed steady-state concentrations of O_3, H_2O_2, and free radicals during ozonation of water at pH 4 to 12. (Governing Eq. 1-4; rate constants as shown in Table 1).

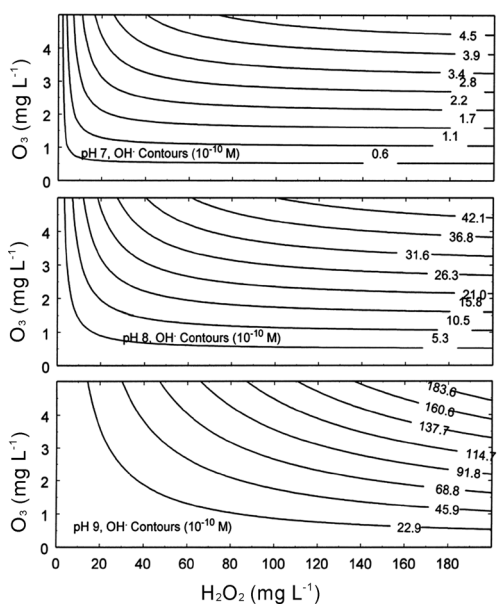

Fig. 4. Computed steady-state OH• concentration for pH 7, 8, and 9. (Governing Eq. 5; rate constants as shown in Table 1.)

■ When H_2O_2 is not added but formed during ozonation as a reaction intermediate, the concentrations of individual $HO_2\bullet/O_2\bullet^-$, $HO_3\bullet/O_3\bullet^-$, $\bullet OH/O\bullet^-$ and H_2O_2/HO_2^- can be computed by solving Eqs. 1-4 simultaneously for different pH values.

The computed concentrations of reactive free-radical intermediates without and with added H_2O_2 are shown in Fig. 3 and 4, respectively.

RESULTS AND DISCUSSION

When MTBE in water is subject to ozonation, it undergoes degradation either by attack of the dissolved O_3, or by attack of the •OH free radical concomitant with O_3 in water. If ozonation is provided via sparging, stripping of MTBE is also a mechanism of removal. The rate of MTBE degradation is:

$$\frac{-d[MTBE]}{dt} = k_{O3\text{-}MTBE}\,[O_3]\,[MTBE] + k_{OH\text{-}MTBE}\,[OH]\,[MTBE] \quad (6)$$

where $k_{O3\text{-}MTBE} = 0.14\ M^{-1}\ s^{-1}$ and $k_{O=H\text{-}MTBE} = 1.9\times10^9\ M^{-1}\ s^{-1}$ are second-order rate constants for the reactions of MTBE with O_3 and •OH, respectively [22]. While treatment of MTBE by O_3/H_2O_2 via the •OH radical is viable, treatment by molecular O_3 alone is not effective. This can be understood from the relative rates of degradation contributed by the 2 different modes with typical doses during ozonation, as shown in Eq. 6. Under typical ozonation conditions (e.g., 1% ozone, pH 7, 25 °C), dissolved ozone in the aqueous phase is typically of several parts per million, according to Henry's Law:

$$C_{O3} = K_H P_{O3} = 9.4\times10^{-3}\ M\ atm^{-1}\ (0.010\ atm) = 0.94\ mM\ (4.5\ mg\ L^{-1}) \quad (7)$$

where C_{O3}, K_H, and P_{O3} are aqueous O_3 concentration at equilibrium, Henry's Law constant (25 °C), and partial pressure of O_3 in the ozone gas stream, respectively. It should be noted that the actual steady-state concentration of O_3 is likely to be slightly lower than its saturation concentration because of continuous decomposition of O_3 in water. The •OH radical is extremely reactive and rather indiscriminant toward species it reacts with, thus the steady-state concentration of •OH radicals in the solution will hardly exceed the order of 10^{-12} M in the presence of O_3 and H_2O_2. Thus, Eq. 6 can be modified under typical O_3/H_2O_2 treatment conditions (assuming $[O_3] = 5\ mg\ L^{-1}$ and $[\bullet OH] = 10^{-12}$ M) to estimate the amount of MTBE degradation by molecular O_3 relative to that by the secondary oxidant •OH free radical:

$$\frac{-d[MTBE]}{dt} = k^1_{O3\text{-}MTBE}\,[MTBE] + k^1_{OH\text{-}MTBE}\,[MTBE] \quad (8)$$

where $k^1_{O3\text{-}MTBE} = 1.4\times10^{-5}\ s^{-1}$ and $k^1_{OH\text{-}MTBE} = 1.9\times10^{-3}\ s^{-1}$ are pseudo first-order rate constants for reactions of MTBE with O_3 and •OH, respectively, assuming $[O_3]_{ss} = 5\ mg\ L^{-1}$ and $[OH]_{ss} = 10^{-12}$ M. Thus, the half-life of MTBE during treatment will be 14 h based on degradation by molecular O_3 or 6 min based on degradation by •OH. This shows that when O_3/H_2O_2 is employed for treatment, •OH free radical will be primary-

Table 2. Comparison of MTBE removal using different treatment conditions, all treatments completed in 36 min. (Liquid volume = 11 L, reactor volume = 13.2 L)

Treatment	Initial [MTBE] (mg L^{-1})	Removal (%)
(a) O_3	12.6	15.2
(b) O_3/H_2O_2 (dosed $[H_2O_2]$ = 14.2 mg L^{-1})	10.6	26.8
(c) O_3 with pressure cycles	11.1	11 (30 cycles; 12 min)
		46 (60 cycles; 24 min)
		56 (90 cycles; 36 min)
(d) O_3/H_2O_2 with pressure cycles (dosed $[H_2O_2]$ = 14.2 mg L^{-1})	11.2	23 (10 cycles; 4 min)
		38 (20 cycles; 8 min)
		45 (30 cycles; 12 min)
		69 (60 cycles; 24 min)
		90 (90 cycles; 36 min)

Notes on experimentation:

(a) MTBE-spiked water was bubbled with an O_3 gas stream containing 16 mg L^{-1} O_3 at 8 L min^{-1} via a gas diffuser. Once the aqueous O_3 concentration reaches 2 mg L^{-1} in 6 min, ozonation was stopped and the reaction allowed to continue for 30 min with stirring. Aqueous O_3 concentration at the end was 1.5 mg L^{-1}.

(b) MTBE-spiked water was dosed with H_2O_2 and then bubbled with O_3 as described above.

(c) MTBE-spiked water in the closed reactor was compressed with O_3 gas stream containing 1.25 mg L^{-1} O_3 at a maximum rate of 60 L min^{-1} through the reactor bottom to reach 690 kPa in the reactor headspace within 20 s, and once reaching the target pressure, the reactor was vented at the top to ambient pressure in 5 s; this compression-decompression cycle was completed for a total of 90 cycles in 36 min. Samples were taken at the end of cycles.

(d) MTBE-spiked water was dosed with H_2O_2 and treated with pressure cycles as described above.

ly responsible for the degradation of MTBE.

It should be emphasized that even when O_3 alone is employed for treatment, the active species responsible for MTBE degradation would still be •OH radical. According to Figs. 3 and 4, the estimated steady-state •OH concentrations are to be 1×10^{-10} M and 2×10^{-12} M, with and without the addition of H_2O_2, respectively. Even at the reduced steady-state concentration at 10^{-12} M without H_2O_2 addition, the •OH free radical would still be more significant than molecular O_3 and be the predominant species for MTBE degradation.

Table 2 compares ozonation treatment results of MTBE without and with the addition of H_2O_2. As shown, MTBE was removed by 15 and 27% with O_3 and O_3/H_2O_2, respectively. The degradation of MTBE by molecular ozone alone is expected to be only 2.5% based on the reported rate constant and assuming 5 mg L^{-1} of O_3 throughout the reaction. Thus, the 15% removal of MTBE would include degradation contributed by •OH and other free radicals while O_3 decomposed in water (as in k_1 and k_7 steps of Fig. 2 that subsequently lead to •OH and others). When H_2O_2 was dosed initially at 14 mg L^{-1}, the removal of MTBE was increased to 27%. This would be consistent with an increased production of •OH free radical by accelerated decomposition of O_3 into hydroxyl and other free radicals, resulting in enhanced degradation of MTBE.

Once the kinetics of MTBE degradation was established for O_3 and O_3/H_2O_2 with conventional gas diffuser in the employed apparatus, the new method based on applying pressures in cycles was tested for enhanced treatment of MTBE. The method involves:

- Pressurizing the water being treated with an ozone/ air mixture through the reactor bottom to an elevated pressure (e.g., 1030 kPa) in the headspace. This is the compression stage.
- When the target pressure is reached, ozone/air pressurization ceases and the pressure is released by venting. This is the decompression stage.
- The compression-decompression ozonation cycle is repeated as necessary for sufficient degradation of the contaminants.

Table 2 compares the treatment results using the pressure cycles with and without the addition of H_2O_2. Ozonation with pressure cycles up to 90 cycles completed in 36 min was compared to conventional ozonation by bubbling for the same duration. As shown, ozonation with pressure cycles heightened MTBE removal, increasing it to 56% removal from 15% without H_2O_2 addition and increasing it to 90% removal from 27% with H_2O_2 addition. The effectiveness can be compared in terms of the O_3 utilization rate (mol MTBE degraded mol^{-1} of O_3 introduced into the reactor). Such comparison yields a utilization rate of 0.15% using O_3 in comparison to 2.2% using O_3 with pressure cycles and 0.22% using O_3/H_2O_2 in comparison to 3.4% using O_3/H_2O_2 with pressure cycles. This means that ozone utilization rate increases by 15 times in both cases when the pressure cycles are used.

The effects of MTBE and H_2O_2 concentrations on removal were examined. Figure 5 shows the remaining fraction of MTBE as it was treated by ozonation with increasing pressure cycles. While the initial MTBE concentration was varied from 12 ppb to 12

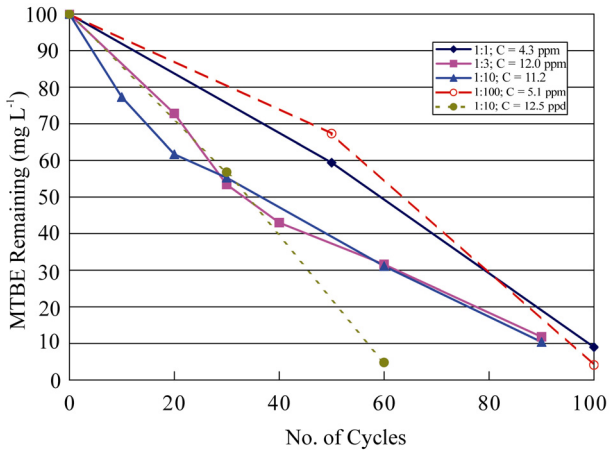

Fig. 5. Degradation of MTBE according to concentrations and numbers of pressure cycles.

ppm and H_2O_2 dosed from 1.4 to 140 mg L^{-1}, the rate of MTBE removal did not vary significantly with the H_2O_2 dosage, but slightly with the initial MTBE concentration. The MTBE concentration was reduced by 90% over 90 or 100 cycles. However, the concentration profiles during the course of reaction did not show the curvature indicative of simple first- or second-order kinetics. Rather, they appeared to be linear resembling zeroth-order. It should be noted that in the low-concentration case of 12 ppb, MTBE was non-detectable (< 1 ppb) after 80 cycles. This is consistent with •OH being the reactive species; the rate of •OH production under the specific reaction conditions determines its steady-state concentration, which in turn determines the rate of MTBE degradation. The presence of added H_2O_2 speeded up the reaction significantly (as shown in Table 2); however, varying the dose of H_2O_2 did not significantly influence the reaction rates. This is consistent with the AOP kinetic model that suggests the maximum steady-state concentration of •OH will depend on an optimal ratio of O_3/H_2O_2 rather than on H_2O_2 concentration alone (see Fig. 4). Thus, increasing available •OH for reaction requires optimal O_3/H_2O_2 ratio, which, however, is likely limited by the steady-state O_3 concentration that can be attained in water in the midst of multiple pathways that deplete O_3.

Pressure is a relevant parameter when applying ozone via pressure cycles, as it will determine the amount of dissolved O_3 and air, which will determine the availability of O_3 as well as the extent of degassing during decompression. Figure 6 shows the effect of varying pressure 480-900 kPa on MTBE removal. As shown, pressure in the tested range has no significant effects on the rate of MTBE removal. It should be noted that the concentration of O_3 available for reaction is subject to the pressures and cycles used. Figure 7 shows the buildup of aqueous O_3 concentration in water (without MTBE or H_2O_2) as it is ozonated at different pressures.

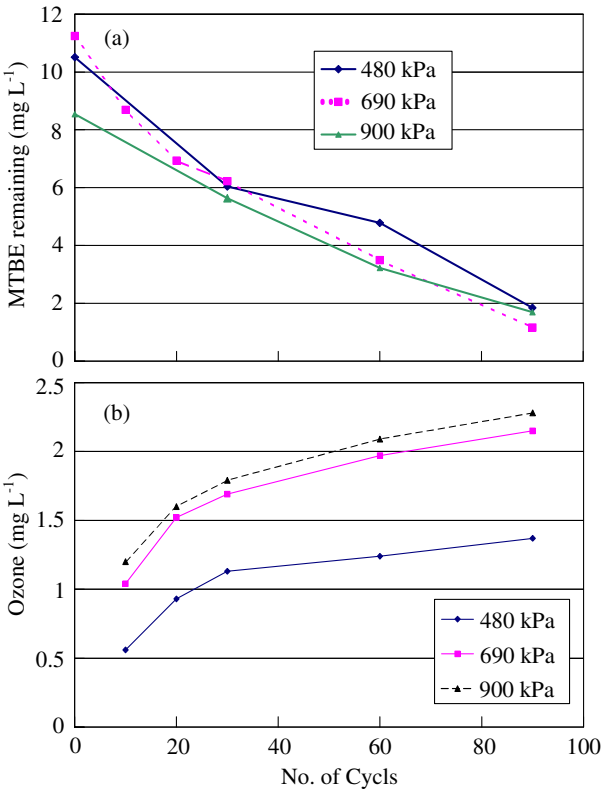

Fig. 6. Degradation of MTBE according to pressure and number of cycles.

Stripping vs. Degradation

Ozonation via a diffuser or compression cycles involves passing a large amount of air through the water, which may result in stripping of MTBE rather than degradation. Experiments were conducted in which known flow rates of air and air containing ozone were passed through the MTBE solution using a gas diffuser and the results of MTBE removal were compared to those of air and air containing ozone using pressure cycles to assess of relative roles of stripping and degradation. Table 3 compares the results. As shown, a high flow of air at 8 L min^{-1} sparged into the water via a gas diffuser tube was capable of removing 7% of the MTBE from solution in 36 min. Thus, stripping could account for up to half of the 15% of MTBE removal when O_3 was used. In comparison, 90 pressure cycles with air removed 25% MTBE, which again could account for up to half of the 56% removal when O_3 was used. It is noteworthy that because of the more effective mass transfer offered by microbubbles formed in pressure cycles, stripping of MTBE became much more pronounced. This was particularly obvious when only half of the total volume of air was used in compression cycles (135 vs 288 L) that resulted in over 3 times as much of MTBE removal. Although up to half of MTBE removal could potentially result from stripping rather than degradation, this was not confirmed by experi-

Table 3. Roles of stripping and degradation in MTBE removal

	Initial [MTBE] (mg L^{-1})	Removal (%)
Air with diffuser at ambient pressure (8 L min^{-1} for 36 min; V_{total} = 288 L)	17.4	
Ozonation with diffuser at ambient pressure (16 mg L^{-1} O_3 at 8 L min^{-1} for 36 min; V_{total} = 288 L)	12.6	15
Air with pressure cycles (90 cycles of air in 36 min; headspace = 2.2 L; V_{total} = 135 L)	16.4	25
Ozonation with pressure cycles (90 cycles of ozone (1.25 mg L^{-1}) in 36 min; headspace = 2.2 L; V_{total} = 135 L)	11.1	56

Note: V_{total} = total volume of air that passed through MTBE-spiked water.

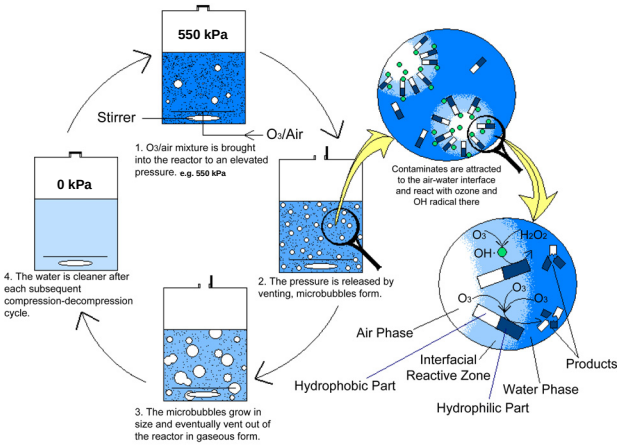

Fig. 7. Proposed mechanism for heightened contact between contaminant and treatment agents that leads to accelerated treatment.

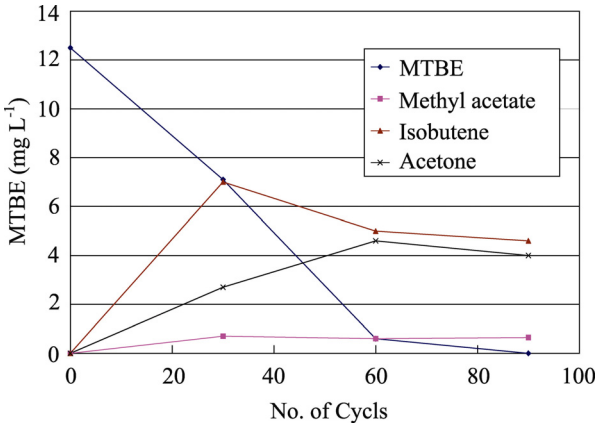

Fig. 8. Disappearance of MTBE and appearance of intermediate during treatment by O_3/H_2O_2.

ments to MTBE in the outlet air. As a result of reactivity and a shortened lifetime of the contaminant in the aqueous phase and possibly in the gas phase when O_3 is present, it is conceivable that stripping may play a lesser role and that the stripped amount is less. This would require further assessment. As in treatment of volatile compounds by ozonation via sparging of O_3, steps should be taken to ascertain the relative roles of stripping and degradation to avoid inadvertent release through effluent gas.

Model of Heightened Reactivity

The heightened degradation of MTBE by O_3/H_2O_2 in the presence of microbubbles is attributed to ample reactive interfacial zone provided by the microbubbles, as illustrated in Fig. 8. The heightened treatment of contaminants by pressure-assisted ozonation has been proposed [28]. Acting like surfactants, the gas-liquid films around the microbubbles provide favorable partition zones that extract and concentrate the hydrocarbon contaminant MTBE there and through this film the now oversaturated ozone will migrate across into the growing O_3-rich gas bubbles. The confluence of O_3 and MTBE at the interface has resulted in the accelerated removal of MTBE. The stripping of MTBE via microbubbles would have occurred and contributed to removal as experiments with air showed. It is conceivable that MTBE may undergo degradation in the presence of O_3/H_2O_2 within the gas bubbles; however, this is not confirmed by experiments as trapping of the rapidly venting effluent gas for analysis has not been completed.

Pathways and Intermediates

Intermediates during degradation of MTBE were monitored and methyl acetate, acetone, and isobutene were found (Fig. 9) in which intermediate were seen to arise and then abate. Methyl acetate and acetone have been well observed in the literature [20,22,23] and are consistent with free radical pathways of degradation such as via:

$$(CH_3)_3COCH_3 + \bullet OH \rightarrow (CH_3)_3CO\bullet + H_3COH$$

$$(CH_3)_3CO\bullet \rightarrow (CH_3)_2CO \text{ (acetone)} + \bullet CH_3$$

and

$$(CH_3)_3COCH_3 + \bullet OH \rightarrow (CH_3)_3CO\bullet + H_3COH$$

$$(CH_3)_2CO \rightarrow CH_3COOH + HCHO$$

$$CH_3COOH + H_3COH \rightarrow CH_3COOCH_3 \text{ (methyl acetate)} + H_2O$$

Isobutene as reaction intermediate has not been observed. Isobutene is the feedstock for production of butyl rubber and is also the intermediate in the manufacturing of MTBE. Bhat et al. contemplated isobutene to be a product of unimolecular decomposition of MTBE [29]:

$$(CH_3)_3COCH_3 \rightarrow (CH_3)_2CCH_2 \text{ (isobutene)} + H_3COH$$

or via free radical reactions:

$$(CH_3)_3COCH_3 + \bullet OH \rightarrow (CH_3)_3COCH_2\bullet + H_2O$$

$$(CH_3)_3COCH_2\bullet \rightarrow (CH_3)_3C\bullet + H_2CO$$

$$(CH_3)_3C\bullet + \bullet OH \rightarrow (CH_3)_2CCH_2 \text{ (isobutene)} + H_2O$$

CONCLUSIONS

In this study, we have found that the removal of MTBE by O_3 and O_3/H_2O_2 is accelerated when ozone is introduced with rapid, successive pressure cycles and removal increases with increasing number of pressure cycles. The heightened kinetics is attributed to abundant gas-liquid interface with the microbubbles that are formed during the degassing stage of the pressure cycles. The removal of MTBE is more effective with O_3/H_2O_2 than with O_3 alone, affirming the role of •OH free radical as the primary oxidant. When H_2O_2 is used, only a small amount is needed and the employed mole ratio of O_3/H_2O_2 is not critical. Stripping may account for up to half of the MTBE removal; however, the amount of stripped MTBE in the reactive gaseous outlet remains to be determined in order to determine the portion due to stripping. The use of pressure cycles during ozonation has resulted in more extensive removal and/or shortened contact time; thus, it has shown potential in enhancing process economics. The process may be applicable toward treatment of other waterborne contaminants.

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CHAPTER 4

DEGRADATION OF EDCs AND PPCPs BY OZONE AND HYDROGEN PEROXIDE

4.1 Abstract

The ubiquitous presence of trace endocrine disruptor compounds (EDCs) and pharmaceutical and personal care products (PPCPs) in the environment is a significant concern. While implications of these compounds on ecosystems and human health are being determined, there has been increasing interest in their treatment such as by tertiary processes at wastewater treatment facilities to arrest their further release to the environment.

The objective of this research has been to study the pressure-assisted ozonation (PAO) technique with or without hydrogen peroxide for the treatment of six selected EDCs and PPCPs, including dibutyl phthalate (DBP), diethyl phthalate (DEP), dimethyl phthalate (DMP), di(2-ethylhexyl) phthalate (DEHP), bisphenol A (BPA), and triclosan (TCS). The effects of oxidant dosage (O_3 and H_2O_2), contaminant concentration, contact time, compression pressure, pH and other treatment conditions on degradation of these contaminants were examined to characterize the new method.

The results showed rapid degradation of the target contaminants and that the new technique possessed potential for removing contaminants more efficiently than

conventional ozonation process. TCS and BPA were readily degraded by O_3 that they disappeared within 6 min from initial concentrations of 8.6 and 9.3 mg/L, respectively. PAO process achieved 45-98% degradation of the study phthalate esters from initial concentrations of 6.9-8.6 mg/L within 24 min, improving by 15-25% over conventional ozonation process. Degradation of the target compounds was favored by increased pressure cycles and increased O_3 concentration, while only marginally improved (5%) by addition of H_2O_2 or increased pressure cycles beyond 60 times.

4.2 Introduction

The target EDCs and PPCPs chemicals in this study were selected on the basis of their frequencies of occurrence in water systems [1], their detrimental effects on human health and ecosystem, and their recalcitrance to conventional treatment processes. The nomenclature, uses, and categories of these six chemicals are shown in Table 4.1. Their structures are shown in Figure 4.1.

BPA is a plastic monomer, 90% or more of it is used for the production of polycarbonate and epoxy resins, unsaturated polyester-styrene resins, flame retardants and other plastics [9]. BPA is produced worldwide with a global capacity of 2,214,000 metric tons in 2003 [10]. It is among the top 31 EDCs detected in drinking waters of North America [11]. The concentrations of BPA in surface water and municipal wastewater treatment plants range from several ng/L to several μg/L [12-13]. The 2003-2004 National Health and Nutrition Examination Survey conducted by the Centers for Disease Control and Prevention found detectable levels of BPA in 93% of urine samples from 2517 people of age 6 and older [14]. As an EDC, BPA has potential to affect human

Table 4.1. Selected EDCs and PPCPs for treatment study

Chemical name	Use	Category
Bisphenol A (BPA)	Used in the production of polycarbonate and epoxy resin; antioxidant in some plasticizers	EDCs and PPCPs [2-3]
Dibutyl phthalate (DBP)	Plasticizer	EDCs [4]
Diethyl phthalate (DEP)	Plasticizer	EDCs [5]
Dimethyl phthalate (DMP)	Plasticizer; Insect repellants	EDCs [6]
Di(2-ethylhexyl) phthalate (DEHP)	Plasticizer	EDCs [7]
Triclosan (TCS)	Preservatives and antioxidants; Disinfectant	PPCPs [8]

reproduction and development; low doses of BPA (50 mg/kg/day) have been reported capable of altering brain chemistry and structure, behavior, immune system, enzyme activity, and the male and female reproductive system in a variety of animals [10]. It is chronically toxic to daphnids because of its ability to interfere with ecdysteroid/juvenoid regulated processes [15]. Various treatments for BPA were attempted including biodegradation by microorganisms [2], anaerobic biotransformation [16], ultrasonic cavitation [17], photodecomposition on nanometer-sized TiO_2 thin film [18], electrochemical treatment via electrochemically generated Fenton's reagent [19], electrochemical oxidation using carbon fiber electrode [20], activated carbon sorption [21], as well as UV photolysis and other AOPs [22].

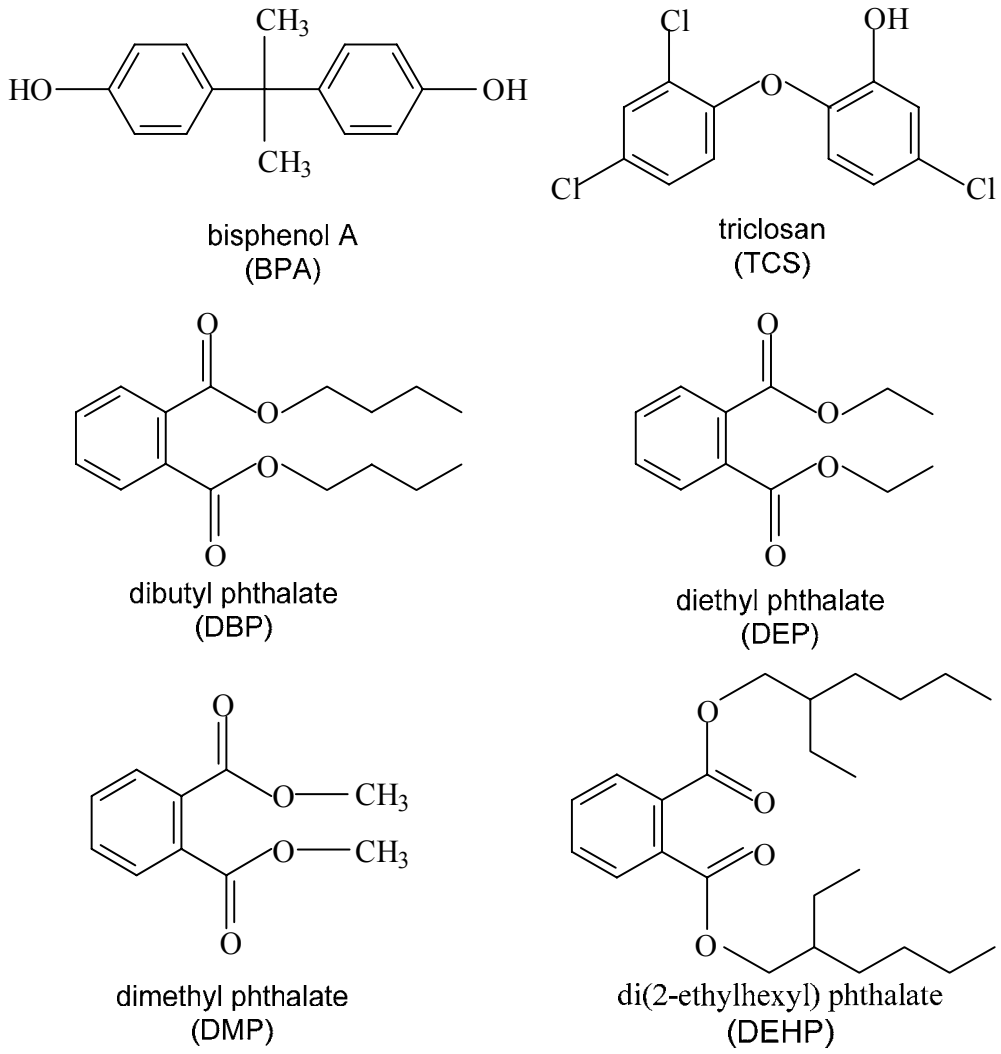

Figure 4.1. Structures of selected EDCs and PPCPs compounds

TCS is an important bactericide and preservative used in various personal care products such as shampoo, soap, tooth paste, cosmetics, skin care lotions, and consumer products such as footwear, carpet, and plastic wear. The compound has been detected in wastewater (from several ng/L to several mg/L), surface water, and sediments [23]. TCS enters the environment mainly through daily use of personal care and other consumer products. Darius Sabaliunas et al. found extensive removal of TCS during wastewater

treatment, with 95% removal at both advanced trickling filter and activated sludge. Another study showed 79, 15, and 6% removals of TCS via biological degradation, sorption to sludge, release into the receiving water, respectively [24]. In rivers, TCS could decline to low concentrations through photolysis and biodegradation [25]. However, TCS may transform into methyl triclosan by biological methylation, which is relatively stable toward photodegradation and can accumulate in organisms [23]. TCS was found to degrade in aerobic soil with a half-life of 18 d, but to persist in anaerobic soil for 70 d [26]. As an antibiotic, TCS is toxic to certain algal species, i.e., *Scenedesmus subspicatus* [24], in which cell glycolysis in suspension or biofilm was inhibited by TCS at 0.1 mmol/L at pH 7 [27]. TCS was linked to a variety of health effects including skin irritation, allergy susceptibility, and hypothermic and depressant effects on the central nervous system of mice [28]. TCS is acutely toxic to grass shrimp and phytoplankton in marine estuarine at several hundred micrograms per liter [29]. Carcinogenic chlorinated by-products can be generated by reactions of TCS with chlorine [8]. Removal methods for TCS include photolysis by natural and artificial UV illumination with a half-life of 20 min [30-31], nanofiltration (NF), reverse osmosis (RO) [32], reaction with ozone with a rate constant of $1.3\times10^{3}\ M^{-1}S^{-1}$ [33], electro-Fenton degradation with hydroxyl radical as the primary oxidant [34].

The four phthalate esters studied are DBP, DEP, DMP and DEHP. Phthalate esters are commonly used as plasticizers that have recently been found to affect endocrine systems in both wildlife and humans [35]. They are also used in industrial solvents, lubricants, hygiene products, cosmetics, as additives in the textile industry and in pesticide formulations [36]. Worldwide production of phthalate esters is 4.3 M ton, with

DEHP accounting for half of it [37]. Phthalate esters are not chemically bonded in host polymers and thus can leach from the product or during the manufacture process into the environment [38]. DBP, DEP, and DEHP are three most frequently detected phthalate esters in environmental samples [37], [39].

DBP is an important additive in special paints and adhesives; it is stable in the natural environment and undergoes slow biodegradation over several days to months [4]. DEP is widely used in the perfume industry; its concentration in many cosmetics products is even higher than a few percents. Long-term exposure to DEP can lead to serious health problems such as reproductive system failure and ocular damage [5]. DMP is the simplest and one of the most commonly used phthalate esters, its metabolite mono-methyl phthalate is not only toxic but also an endocrine disruptor. Under aerobic conditions, DMP can be removed in less than 5 days in a wastewater treatment plant; under anaerobic conditions it is degraded much slower, usually more than 10 days [6]. DEHP mainly serves as a plasticizer in polyvinyl chloride plastics to impart flexibility, strength, temperature tolerance, and stability. Due to its wide uses, DEHP is detected in all environmental samples including air, water, sediment, and soil. Exposure to DEHP produces a variety of adverse effects in experimental animals in the forms of cancer, liver damage, and reproductive system alterations [7]. Removal methods for phthalate esters include photocatalytic degradation [40], active carbon adsorption [41], adsorption by molybdate impregnated chitosan beads [42], biodegradation [43-46], wetland system [47], gamma ray irradiation [48] and advanced oxidation process [49].

Pressure-assisted ozonation (PAO) is a novel technique. It incorporates rapid, successive cycles of compression and decompression during ozonation, facilitating

generation of numerous ozone microbubbles within the water being treated. These ozone-containing bubbles grow and expand during the decompression step and provide reactive zones at the gas–liquid interface, resulting in heightened contact between the O_3 molecules, free radicals and target chemicals. In this research, the application of PAO for the removal of 6 target EDCs and PPCPs was demonstrated. We tested the effects of different PAO treatment parameters on the degradation of these 6 selected chemicals, and compared the results with those of the conventional ozonation.

4.3 Experimental

4.3.1 Reagents

BPA (purity ≥97%), DBP (purity ≥99%), DEP (purity ≥99.5%), DMP (purity ≥99%), DEHP (purity ≥99%), and TCS (purity ≥97%) used in this study were purchased from Sigma Aldrich (USA, MO) and used as received. Acetone (purity ≥99.5%), dichloromethane (DCM; purity ≥99.5%), sodium hydroxide, sodium phosphate, sodium borate, sodium bicarbonate were purchased from Mallinckrodt Baker (USA, NJ). Sodium carbonate and phosphoric acid were from EMD Chemicals (USA, NJ). Sulfuric acid (purity 95-98%), potassium indigo trisulfonate were purchased from Sigma Aldrich (USA, MO). All the water used was distilled water. Stock solutions of selected chemicals were prepared in acetone, stored at 4 °C and renewed monthly.

4.3.2 Methods

The experimental setup for the treatment of target EDCs and PPCPs in water by PAO is shown in Figure 4.2. It consisted of a gas tank (containing either air or oxygen) as

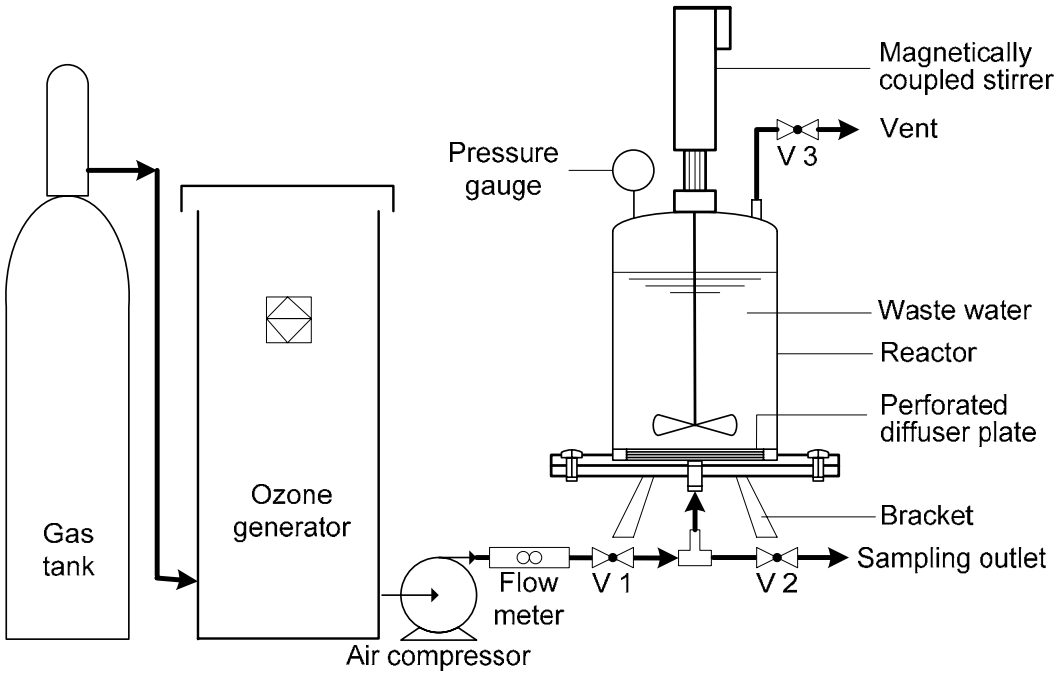

Figure 4.2. Pressure reactor and experimental setup for EDCs and PPCPs treatment

the feed gas for ozone generation, an ozone generator, an air compressor, a stainless reactor and a pressure gauge, a flow meter, stainless steel pipes as well as valves. The reactor was coupled with a magnetic stirrer for better contact of the ozone/air mixture with the contaminated water. The reactor volume was 1.8 Liters. It was constructed of two stainless-steel pieces with a wall thickness of approximately 1 cm, which was held together by three bolts to form the reactor. The reactor had a perforated diffuser plate, additional inlet and outlet at the bottom, and vents on the top with control valves. Compression of the ozone/air mixture was achieved through the bottom entrance, while decompression was through gas vent at the top. The stock solution of the six chemicals was about 3000 mg/L acetone solution. Each time 1 mL of this stock solution was added to the reactor, after all the acetone had evaporated, 400 mL distilled water were added to the reactor and stirred for 10 min for mixing.

In this PAO experiment, the compression time was 67~69 s and decompression time was 3~5 s for each cycle. The compression-decompression cycle could be repeated rapidly for as many times as necessary for the sufficient degradation of any contaminants. At the end of each single experiment, all the reacted solutions were collected to be extracted by DCM.

4.3.3 Chemical analysis

A GC/MS procedure was used to analyze the target EDCs and PPCPs compounds. The preparation procedures included liquid-liquid extraction of spiked water by DCM in accordance with EPA METHOD 3510C [50]. The reactor wall and stirrer were rinsed by DCM for three times and the elution was collected and combined with the extraction.

The final concentration of the extraction was first conducted by rotator evaporator and then by N_2 gas purging.

The pretreated samples were analyzed by GC/MS analysis quantitatively and qualitatively. The program of the GC/MS was as follows: a 2 μL sample was injected into a capillary column (HP-5MS, Agilent), the temperature of inlet was 250°C. Helium was the carrying gas with a gas flow rate of 45 cm/sec. The oven temperature was kept at 60 °C for 1 min, then increased to 100°C at the rate of 20°C/min, and from 100°C to 300°C at 5°C/min, and finally kept at 300°C for 5 min. The mass spectra were set in scan mode from 50 to 500 m/z, and the interface temperature was 300°C. The aqueous O_3 concentration was measured by the Indigo Colorimetric Method [51]. The concentration of H_2O_2 in the water was measured by a HACH Hydrogen Peroxide Test Kit (Model HYP-1).

4.4 Results and discussion

The effect of PAO treatment parameters on spiked EDCs and PPCPs was investigated.

4.4.1 Effect of pressure

The spiked 6 EDCs and PPCPs in this series of experiments were DMP, DEP, DBP, DEHP, TCS and BPA. The reaction conducted under ambient pressure had a reaction time of 24 min, which was the same with the PAO. The PAO treatments of target chemicals were performed separately under varied pressures of 50, 70, and 100 psi.

The results in Figure 4.3 indicate that TCS and BPA were readily degradable by ozonation under both ambient and PAO conditions; both of them were below the detection limit after 24 min ozonation and reached a complete removal. The four phthalate esters were degraded to different extents due to their chemical properties. DMP and DEP were easier to degrade while DEHP was the most recalcitrant phthalate ester, due to its chemical structure with the longest and most complex branch chain among the four phthalates.

All of the six target chemicals contained one or more aromatic rings, which was the nucleophilic position of the molecule that was prone to be attacked by electrophilic agent ozone. In addition, the groups on the aromatic ring tended to activate or deactivate the reactivity of the chemicals. For TCS and BPA, the –OH and –O groups strongly activated the aromatic ring, and the –alkyl group had fairly weak deactivation function. The –Cl groups were also a deactivation group in the TCS molecule; however, their effect was weak.

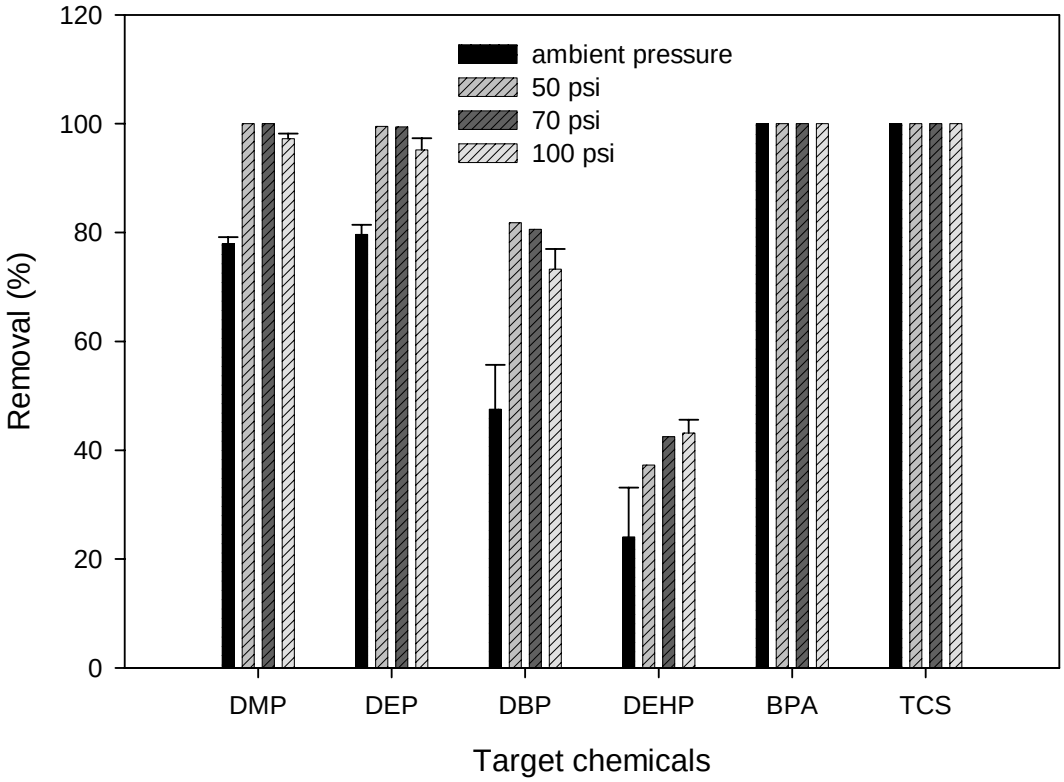

Figure 4.3. Removal of 6 target chemicals at different pressures

(Initial concentration of DMP, DEP, DBP, DEHP, TCS and BPA: 8.6 mg/L, 8.0 mg/L, 6.9 mg/L, 6.9 mg/L, 6.5 mg/L and 6.9 mg/L; Pressure cycles and time: 20 cycles in 24 min; Aqueous O_3 concentration: 16.6 mg/L; H_2O_2/O_3 mole ratio: 1/1)

For the phthalates, the –COOR tended to deactivate the electrophilic substitution reaction [52], and the longer –R made ozonation degradation more difficult.

PAO method was more effective in treating these compounds than traditional ozonation: DMP, DEP, DBP and DEHP got the improved removal of 97.9, 96.7, 75.9 and 44.9% with O_3 and H_2O_2 as the oxidant under PAO conditions (100 psi), compared to the removal of 78.8, 80.9, 53.3 and 30.5% under ambient conditions.

The removals of each phthalate ester were very close under different pressures during PAO processes, according to observations. Higher pressures usually produced more microbubbles than lower pressures. However, a pressure as low as 50 psi could already generate enough microbubbles to make a noticeable difference from the results observed under ambient conditions.

These results supported the explanation that the degradation level and rate of target compounds were essentially related to the microbubbles generated during those compression-decompression cycles, which increased the ozone transfer efficiency. When the O_3 and ·OH concentrations in the whole system were relatively equal, the interfacial board between the gaseous phase and the aqueous phase provided a place where target compounds, O_3 and ·OH congregated in a much higher concentration and reacted to each other more rapidly than when they were in the homogeneous phase.

To further determine the effect of PAO on TCS and BPA, an experiment with less harsh conditions was conducted. The results and conditions are shown in Table 4.2, which indicated that TCS and BPA can be removed to a percentage of greater than 98% in only 6 min under lower pressures and lower ozone concentrations.

The effects of the removal of TCS and BPA in shorter reaction time were not explored in this research. However, the research by Suarez et al. indicated that TCS could be oxidized very rapidly with a half-life of only 0.9 ms for an ozone concentration of 1 mg/L under the condition of pH 7 [33]. BPA has shown a similar property; for an ozone concentration of 1 mg/L, the half-life of BPA was lower than 15 ms [53-54].

Table 4.2. PAO treatment result of TCS and BPA – less harsh conditions

Chemical	Conditions	C_0 (mg/L)	C_f (mg/L)	Removal (%)
TCS	Pressure: 50 psi Pressure cycles: 10 cycles	8.6	<0.12	>98
BPA	Reaction time: 6 min Ozone concentration: 8.9 mg/L No H_2O_2 added	9.3	<0.12	>98

C_0: initial concentration; C_f: final concentration

4.4.2 Effect of ozone concentration

As an oxidant and a treatment agent in the ozonation reaction, O_3 played an essential role in the degradation of contaminants. Thus the effect of O_3 concentrations needed to be studied for the target chemicals degradation by ozonation. In this group of experiments, the PAO experiment was conducted with the O_3 concentrations set to be 5.9 mg/L, 8.9 mg/L and 16.6 mg/L respectively. These O_3 concentrations were used in the previous study of ozonation of organic contaminants such as phthalates and antibiotics [33, 55-58].

The importance of O_3 concentrations is demonstrated in Figure 4.4, which shows that the higher the O_3 concentration, the higher the removal of target chemicals. The removal of DMP, DEP, DBP and DEHP were 74.4, 74.2, 53.3 and 35.6%, respectively with an O_3 concentration of 5.9 mg/L. When the O_3 concentration was increased to 16.6 mg/L, the chemicals removal increased to 97.9, 96.7, 75.9 and 44.9% respectively. Again

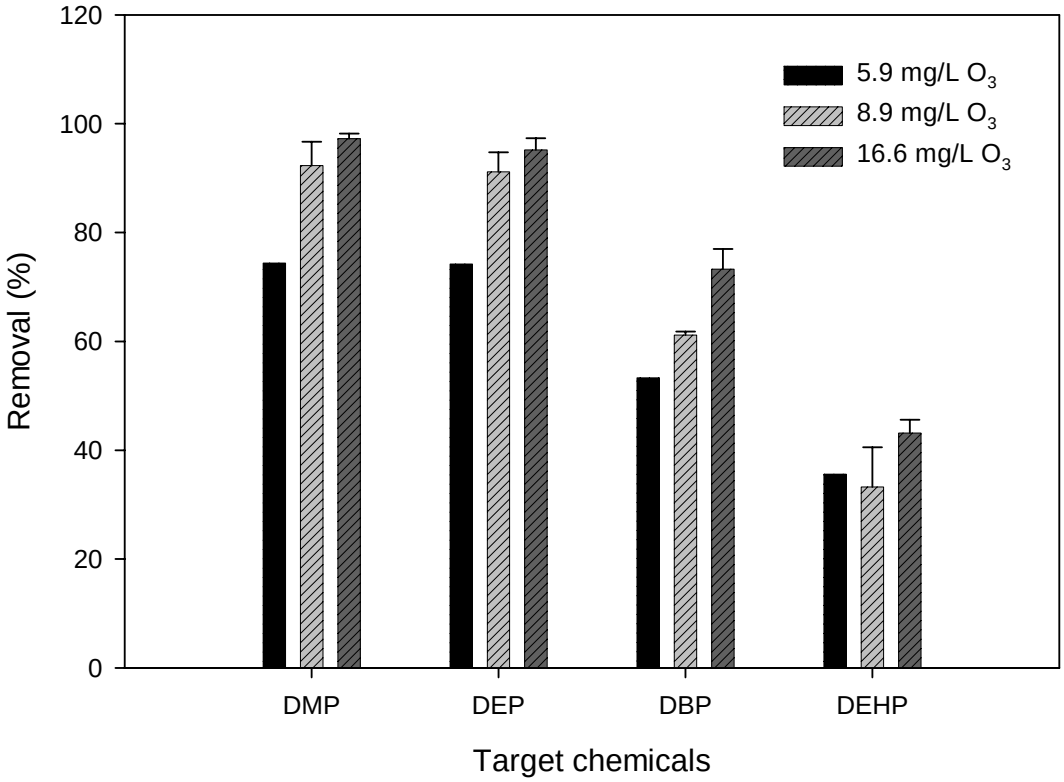

Figure 4.4. Removal of 4 target chemicals at different O_3 concentrations (Cycles: 20 cycles; Compression pressure: 100 psi; H_2O_2/O_3 mole ratio: 1/1; Initial concentrations of DMP, DEP, DBP and DEHP: 8.6, 8.0, 6.9 and 6.9 mg/L)

DEHP proved to be most recalcitrant among the four phthalates, and DBP was more recalcitrant than DMP. This sequence was in accordance with the order of their carbon chain length and molecular weight. The extent of removal in response to varied O_3 concentrations indicated that they were susceptible to electrophile O_3 attack, which showed that they were degraded by O_3 directly. However, the increase in removal was not in proportion to the increase in O_3 concentration, so experimenting with an unlimited increase of O_3 concentration was unwarranted for efficiency and cost consideration.

The removal of phthalates by ozone under ambient pressure had been reported by some other studies with close results to those in this research. Byung et al. found that when using ozone (dose rate at 1.5 mg/L min) as the only oxidant, the DEP (initial concentration of 22.2 mg/L) removal could reach 75% in 30 min [55]. The study of Chen et al. on DMP has shown a similar trend: 77.7 mg/L DMP in the water was removed to 98% by an ozone concentration of 14 mg/L in 30 min and in 60 min by an ozone concentration of 8 mg/L [57].

4.4.3 Effect of H_2O_2/O_3 mole ratio

The H_2O_2/O_3 mole ratio was another important parameter in AOPs treatment because the aid of H_2O_2 was expected to increase the generation of OH radicals, which in turn made it possible to elevate the removal of contaminants more effectively. Here the PAO experiment was conducted with H_2O_2/O_3 mole ratios of 1/2, 1/1, and 10/1, respectively. The results were compared with those when no H_2O_2 was added.

Although the addition of H_2O_2 was expected to greatly promote the decomposition of ozone and push the reaction along rapid indirect way [59], the results in Figure 4.5 indicates the addition of H_2O_2 aided the removal but to a limited degree. A very high H_2O_2 dose was not necessary for the more effective removal of target compounds. This seemed to indicate that the reaction between target chemicals and O_3 was in both direct and indirect ways. When H_2O_2 was not added to the reaction system but formed during ozonation as a reaction intermediate, a small amount of OH radicals would be generated, and the amount of OH radicals depended strongly on O_3 than H_2O_2. The initiators that triggered the decay of ozone might be the OH^- that came from the

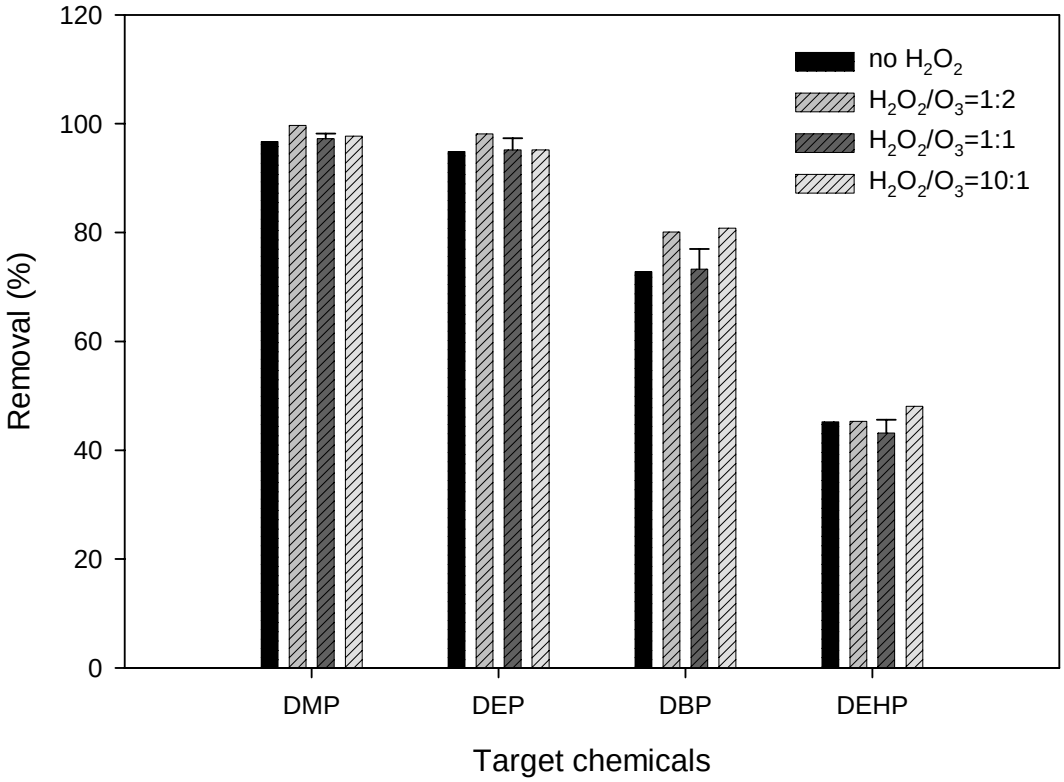

Figure 4.5. Removal of four target chemicals at different H_2O_2/O_3 mole ratios (Cycles: 20 cycles; Compression pressure: 100 psi; Aqueous ozone concentration: 16.6 mg/L; Initial concentrations of DMP, DEP, DBP and DEHP: 8.6, 8.0, 6.9 and 6.9 mg/L)

water used in this experiment. The larger amounts of free radicals generated by the aid of H_2O_2 addition promoted the degradation of target compounds but the degradation rates were relatively independent of the amount of H_2O_2 added. Increasing of the H_2O_2/O_3 mole ratio might produce more ·OH, however this high production of free radicals could also lead to a low reaction rate because these radicals could recombine, which would not be helpful for the oxidation process [60].

Hydrogen peroxide worked not only as an initiator and promoter of the ozonation,

but also acted as an inhibitor of ozone decomposition when its concentration was so high that the H_2O_2/O_3 reaction became mass transfer-controlled [52]. According to this result, a H_2O_2/O_3 mole ratio of 1/2 is the proper ratio. Increasing this ratio does not improve the removal proportionally.

4.4.4 Effect of pressure cycles

To observe the removal rates of target compounds by PAO, the removals of four phthalate esters were measured at pressure cycle numbers of 5, 10, 20, 40 and 60, the corresponding reaction times were 6, 12, 24, 48 and 72 min. The results shown in Figure 4.6 reveal that the four phthalate esters were degraded quickly during the first 10 cycles, slowly after 20 cycles and after 60 cycles their degradation almost ceased, the final removal percentages of the 4 phthalate esters were 100, 100, 85.1 and 60.3%, respectively.

In a contaminant-O_3 reaction system, when the concentration of contaminants decreased to a very low level, the reaction rate decreased accordingly assuming the reaction kinetic constant and the concentration of O_3 were kept the same; pH value was another possible reason for the removal rate slowing down.

In this experiment, the initial pH of the reaction system was 6.7, which was neutral and O_3 and OH radicals could both attack the target compounds to decompose them. After 24 min ozonation, the pH value dropped to 4.3, which was acidic, under this pH level the OH radicals generation nearly stopped, this had an adverse effect on ozonation because under this pH condition the direct ozonation reaction dominated, which involves slow reaction rate constants.

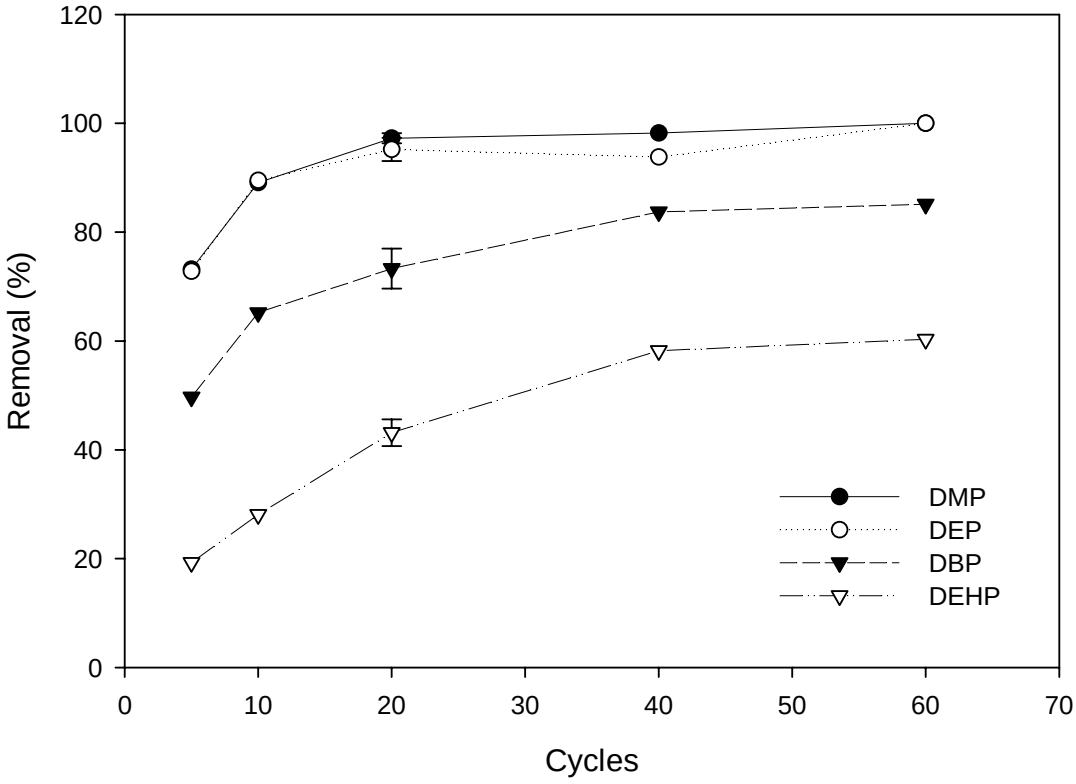

Figure 4.6. Removal rates of 4 phthalate esters at different cycles

(Compression pressure: 100 psi; Aqueous ozone concentration: 16.6 mg/L; H_2O_2/O_3 mole ratio: 1/1; Initial concentrations of DMP, DEP, DBP and DEHP: 8.6, 8.0, 6.9 and 6.9 mg/L)

4.4.5 Effect of pH

The effect of pH on the PAO treatment of target chemicals was worth studying because the pH values often controlled ozonation direction and speed. The ions in the ozonation reaction system that affected the pH might either impede or prompt the generation of relative radicals. Here $NaH_2PO_4 \cdot H_2O$ (0.04 M) and 1:1 H_2SO_4 (0.15 ml)

were used to make a pH 3 buffer solution, $NaH_2PO_4 \cdot H_2O$ (0.05 M) and NaOH (0.03 M) were used to make a pH 7 buffer solution, Na_2CO_3 (0.05 M) and $Na_2B_4O_7 \cdot 10H_2O$ (0.001 M) were used to make pH a 10 buffer solution. H_2O_2 was not added in this group of experiments.

The effect of pH on PAO treatment results is shown in Figure 4.7. It indicates that pH 7 and pH 10 have positive effects on PAO treatment of 4 phthalate esters, while pH 3 has a negative effect. The removal of DMP, DEP, DBP and DEHP were 100, 100, 91.9 and 41.0% when pH was 7. Both pH 7 and pH 10 created a better environment for the degradation of target compounds, because the concentration of free radicals increased with increasing pH so the reaction between target chemicals and ozone was in a rapid indirect way, this result was in accordance with the common conclusion [52, 60]. At pH 3 the phthalates existed mostly in their aliphatic form, which has a low reactivity toward electrophile O_3 attack so that their degradation rates decreased.

The pH 10 buffer solution contains Na_2CO_3, the carbonate and bicarbonate ions, known to be ·OH scavengers, whereas in this group of experiments, the contaminants removal was not negatively affected by the presence of carbonate and bicarbonate. This might be due to two reasons. First, sometimes carbonate ion species are not pure inhibitors, ·OH radicals might react with carbonate ion species to yield carbonate ion radicals, which are active in oxidizing the target chemicals [52]. The other reason was that although carbonate and bicarbonate reduced the decay rate of ozone, they increased the stability of ozone [60] so that ozone could react with contaminants in direct way. The pH 7 buffer system had the same reaction mechanisms, where phosphate acted as ·OH scavenger without adversely affecting the contaminants degradation because the target

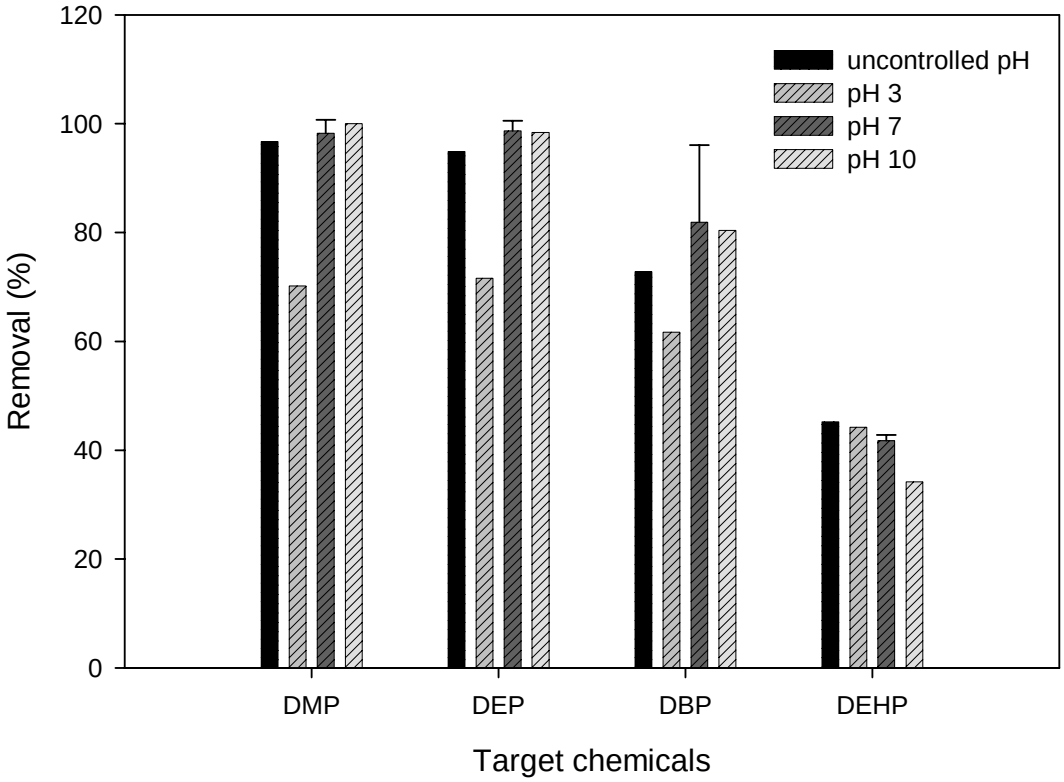

Figure 4.7. Removal of 4 phthalate esters at different pH

(Cycles: 20 cycles; Compression pressure: 100 psi; Aqueous ozone concentration: 16.6 mg/L; Initial concentrations of DMP, DEP, DBP and DEHP: 8.6, 8.0, 6.9 and 6.9 mg/L)

EDCs and PPCPs compounds were reacting with ozone in both direct and indirect pathways. For practical waste water treatment processes pH 7 is a more available and preferable choice.

4.4.6 Effect of initial chemical concentration

Considering the factor that concentrations of EDCs and PPCPs chemicals in the natural samples were usually very low, the effect of the initial target chemicals

concentration on the PAO treatment was investigated and the results are shown in Figure 4.8. Here the high initial concentrations were: DMP, 8.6 mg/L; DEP, 8.0 mg/L; DBP, 6.9 mg/L; DEHP, 6.9 mg/L, the low initial concentrations were: DMP, 87 µg/L; DEP, 106 µg/L; DBP, 117 µg/L; DEHP, 139 µg/L.

The high initial concentrations were nearly 100 times greater than the low initial concentrations. These higher concentrations had a much less pronounced effect on removal percentages with a difference that was no more than 10%. This revealed that in this reaction system when there was a large excess of the ozone, the degradation rates of target compounds depended mainly on their own concentrations in the system. This process could be described by the following kinetic expression:

$$dC_c/dt = -k'C_{O3}C_c = -kC_c \qquad (4.1)$$

Here k' is a 2nd order reaction rate constant, C_{O3} is the aqueous ozone concentration, which could be considered to be a constant, for in this experiment, ozone gas was continuously sparged into the water, which kept the aqueous ozone concentration at a stable level during the reaction (0.35 mM), thus this reaction could be assumed as pseudo-first order, so k was the pseudo-first order kinetic rate constant. C_c was the concentration of target chemicals. Table 4.3 shows the rate constants for ozonation of phthalates by this study and some other studies.

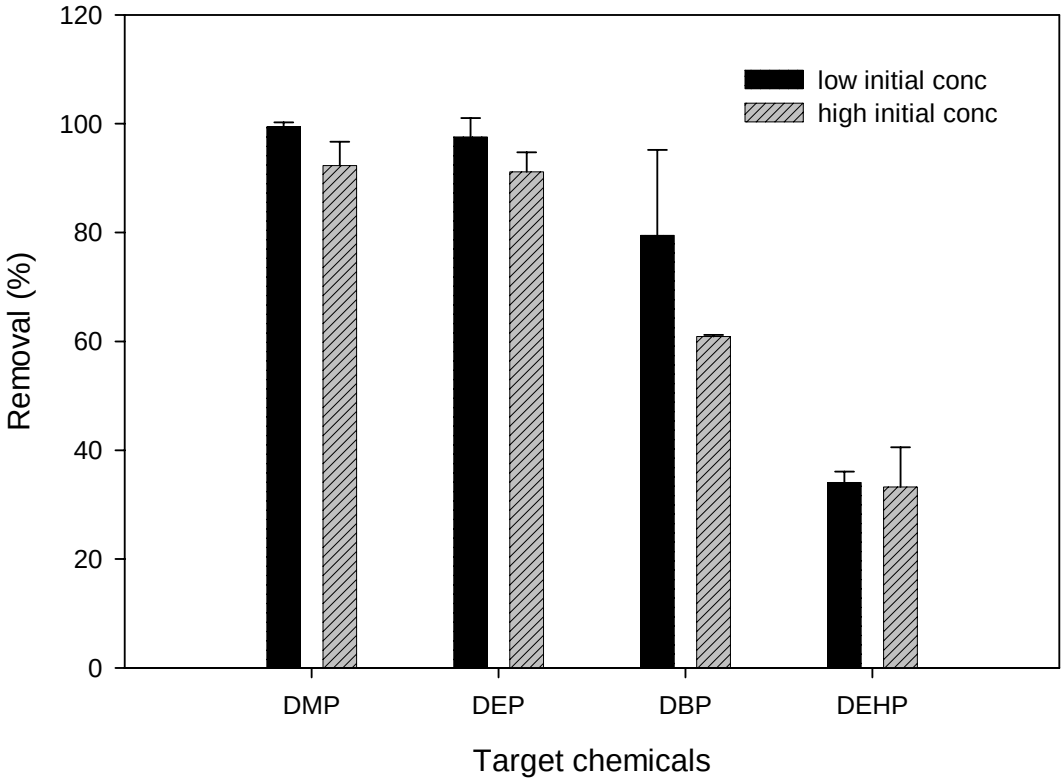

Figure 4.8. Removal rates of four phthalate esters at different initial concentrations (Pressure cycles: 20 cycles; Compression pressure: 100 psi; Aqueous ozone concentration: 8.9 mg/L; H_2O_2/O_3 mole ratio: 1/1)

Table 4.3. Rate constants for ozonation of phthalates

Reaction	Rate constants k (s^{-1})	O_3 conc mM	Treatment condition
DMP with O_3 and H_2O_2	2.6×10^{-3}	0.35	PAO
DEP with O_3 and H_2O_2	1.8×10^{-3}	0.35	PAO
DBP with O_3 and H_2O_2	9.0×10^{-4}	0.35	PAO
DEHP with O_3 and H_2O_2	4.0×10^{-4}	0.35	PAO
DEHP with O_3	1.3×10^{-4}	0.38 *	pH 7 [61]
DEHP with O_3	1.6×10^{-4}	*	pH 11 [61]
DEHP with O_3	2.0×10^{-4}	*	with catalyst Cr(III) [61]

Assuming the reaction to be pseudo-first order, thus $dC_c/dt = -kC_c$, $\ln C_c = -kt$, plot $\ln C_c$ Vs. t to obtain a linear curve, the slope of the linear curve is then fit to be k.

*: Ozone was fed at the rate of 96 mg/min during the whole process.

4.5 Summary

TCS and BPA were readily degradable by ozonation, they disappeared within minutes of PAO treatment. The four phthalates were degraded to different extents due to their chemical structures. DMP had the highest degradability, DEP were the second one, while DEHP had the lowest degradability to ozonation. The resistance to degradation increased with increasing carbon chain length or molecular weight. The chemical structure with long and complex branching of carbon chain as in DEHP makes it most recalcitrant among the four phthalates. Intuitively, the degradation of organic chemicals with similar structures would require similar energy in reaction with ozone along similar

patterns, thus, the degradation results of the selected chemicals by ozone have the potential to reveal the pattern of degradation for other organic contaminants.

PAO process could increase the removal rates of the 4 phthalates by 15~25% compared to normal ozonation process under ambient pressure within the same reaction time. Higher aqueous O_3 concentration led to more effective target EDCs and PPCPs compounds removal. The addition of H_2O_2 promoted the degradation of target compounds but the degradation rates were ralatively independent of the amount of H_2O_2 added. Increasing compression cycles favored the removal of target compounds, however the degradation nearly ceased after 60 cycles. pH 7 and pH 10 had positive effects on PAO treatment of the four phthalate esters, while pH 3 has a negative effect.

4.6 References

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CHAPTER 5

DEGRADATION OF NAs BY OZONE AND HYDROGEN PEROXIDE

5.1 Abstract

Naphthenic acids (NAs) are carboxylic acids and natural components of crude oil; they are released to tailings ponds during oil sands extraction by hot water and eventually enter natural water systems through leaking. NAs are toxic to many aquatic organisms, to eliminate the toxicity of NAs and prevent their damage to ecosystems, measures have to be taken to remove them. This research studied the degradation of two commercially available NAs - Cyclohexaneacetic acid and Cyclohexanebutyric acid, by ozone and hydrogen peroxide. The effects of oxidant dosage, contact time, contaminant concentrations, and the effect of PAO were tested. The results indicated that ozonation was very effective in removing NAs in the aqueous phase, especially with the proper addition of hydrogen peroxide. The combination of high concentrations ozone (14.8 mg/L) and the proper dosage of hydrogen peroxide (H_2O_2/O_3 mole ratio 1/1) could degrade NAs (initial concentration 17 mg/L) completely in only 10 min. Of all the experimental parameters, ozone concentration was the most important. The higher the ozone concentration, the faster the target NAs degrade. PAO could increase the removal percentage of the 2 NAs by about 20%, with other parameters remaining constant.

5.2 Introduction

Studies on the degradation of NAs have been conducted by a number of researchers. Most of this research was focused on biodegradation. Biological treatment was proved to be a feasible way to degrade NAs, although it usually took a period of long time. The research on the removal of NAs by AOPs is very limited. Dena et al. tested the photolysis of NAs by UV/artificial solar radiation, they found the concentrations of neither the individual NAs compounds nor their mixtures were significantly reduced in natural surface water; however, they found some compositional changes occurred within the mixtures, and that UV_{254}-radiation may reduce the concentration of some NAs [1].

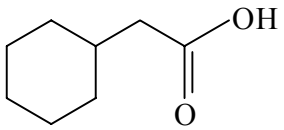
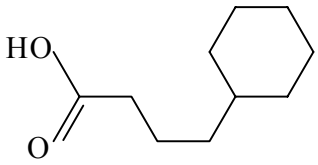
The objective of this research is to study the AOPs degradation of two commercially available naphthenic acids by ozone and hydrogen peroxide. The effects of oxidant dosage, contact time, contaminant concentrations and other parameters were tested. PAO technology was also applied in this research to evaluate its capability to treat NAs. Table 5.1 shows the structure, chemical properties and uses of the 2 chosen NAs.

5.3 Experimental

5.3.1 Reagents

Cyclohexaneacetic acid (purity 99%) and Cyclohexanebutyric acid (purity 99%) used in this study were purchased from Sigma Aldrich (USA, MO) and used as received. Acetone (purity≥99.5%), ammonium hydroxide (28.9~30.0%), formic acid (purity 95%) were purchased from Mallinckrodt Baker (USA, NJ). Methanol (purity≥99.8%) and potassium indigo trisulfonate were purchased from Sigma Aldrich (USA, MO). Stock solutions of selected NAs chemicals were prepared the same as PPCP.

Table 5.1. The structure, chemical properties and uses of 2 chosen NAs

Chemical name	Cyclohexaneacetic acid	Cyclohexanebutyric acid
structure		
Mole weight	142 g/mol	170 g/mol
Solubility	<50 mg/L at pH 7 in water	
pKa	Between 5 and 6	
Uses [2]	Na salts: Emulsifying agent for agricultural insecticides, additive for cutting oils emulsion breakers in the oil industry; Fe and Mn naphthenates: Fuel additives for improved combustion and reduced corrosion; Cu and Zn naphthenates: Wood preservatives	

5.3.2 Methods

The experiments were conducted with the equipment shown in Figure 5.1. This equipment consisted of a gas tank, an ozone generator, a flow meter, an air compressor, and a reactor. The reactor (volume 0.65 L) was made of stainless steel with an inlet leading to the bottom to distribute the ozone/air mixture gas and an outlet at the top of the lid for gas ventilation. The lid could be opened to take samples out.

Usually 1 mL of the NAs stock solutions was added into the reactor. After the acetone had evaporated, 100 mL tap water was added to the reactor and mixed well with the NAs. Ozonation was triggered by introducing the ozone/air mixture into the reactor by an air compressor.

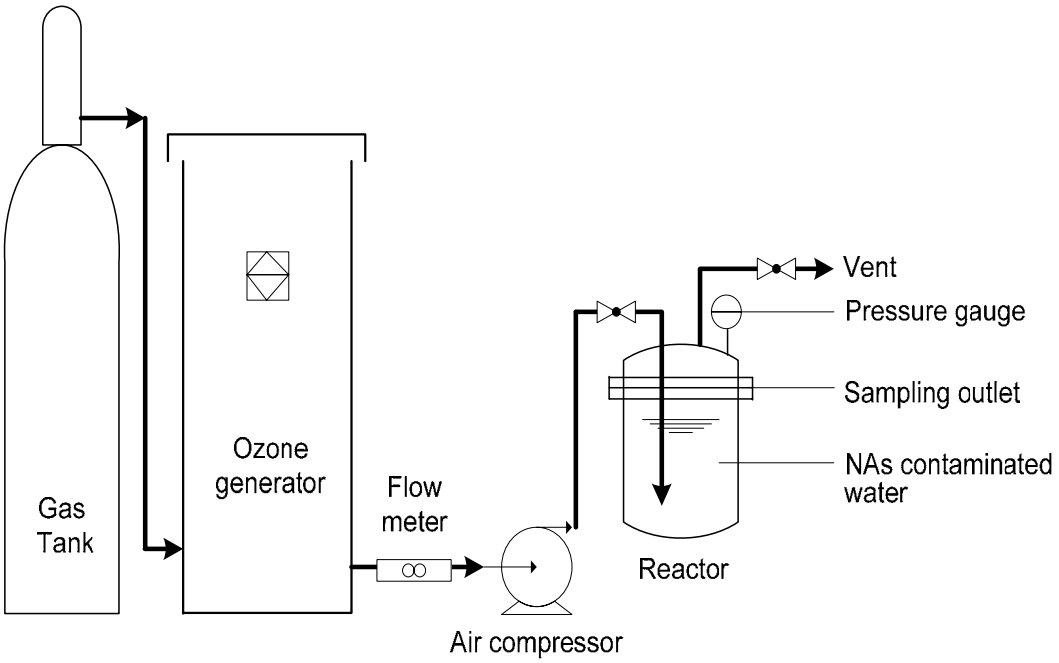


Figure 5.1. Pressure reactor and experimental setup for NAs treatment

H_2O_2 was added as needed before introducing the ozone. The compression and decompression cycles were repeated for a number of times and water samples were taken at regular intervals during each single experiment as necessary, which were measured as shown in 5.3.3.

5.3.3 Chemical analysis

A GC/MS procedure was used to analyze the two target NAs compounds. The NAs were extracted from water by solid phase extraction (SPE) with an Oasis MAX cartridge (Waters Corp.) prior to GC/MS quantitative and qualitative analysis.

During the SPE procedure, the cartridge was first conditioned by 1 mL methanol and equilibrated by 1 mL water, then 10 mL ionized sample (adjust the pH of the sample

to 10 with ammonium hydroxide) was loaded into the cartridge, which was then washed with 2 mL 5% ammonium hydroxide in water and dried by air flushing. The NA on the cartridge was finally eluted by 2 mL 2% formic acid in methanol and the extraction was concentrated to 0.2 mL by N_2 gas purging.

The program of the GC/MS was as follows: a 2μL sample was injected into a capillary column (HP-5MS, Agilent). The inlet temperature was 250°C. The carrying gas was helium and the gas flow rate was 46 cm/sec. The oven temperature was kept at 100 °C for 3 min, then increased to 300°C at the rate of 8°C/min, and finally kept at 300°C for 5 min. The mass spectra were set in scan mode from 50 to 550 m/z.

The aqueous O_3 concentration was measured by the Indigo Colorimetric Method [3]. The concentration of H_2O_2 in the water was measured by a HACH Hydrogen Peroxide Test Kit (Model HYP-1).

5.4 Results and Discussion

Table 5.2 lists the six experiment conditions under which the removal of cyclohexaneacetic acid and cyclohexanebutyric acid by ozone and hydrogen peroxide was performed. In each test, the aqueous ozone concentration, H_2O_2/O_3 mole ratio, reaction time and PAO pressure were varied to study their individual effects on the removal percentage and rate of chosen NAs. Figure 5.2 and Figure 5.3 show the experiment results of cyclohexaneacetic acid and cyclohexanebutyric acid respectively.

Results shown in Figure 5.2 and 5.3 indicate that the two NAs were following similar degradation tendency. The experimental conditions for test 2 was proved to be most effective and that for test 5 was the least effective for the removal of two NAs.

Table 5.2. Experiment conditions for the removal of NAs

No.	Experiment conditions
Test 1	Ozone concentration (aq): 14.8 mg/L; H_2O_2: not added; Pressure: ambient; Initial NAs concentration: Cyclohexaneacetic acid: 16.7 mg/L, Cyclohexanebutyric acid: 16.6 mg/L.
Test 2	Ozone concentration (aq): 14.8 mg/L; H_2O_2/O_3 mole ratio: 1/1; Pressure: ambient; Initial NAs concentration: Cyclohexaneacetic acid: 16.7 mg/L, Cyclohexanebutyric acid: 16.6 mg/L.
Test 3	Ozone concentration (aq): 6.1 mg/L; H_2O_2/O_3 mole ratio: 1/1; Pressure: ambient; Initial NAs concentration: Cyclohexaneacetic acid: 17.3 mg/L, Cyclohexanebutyric acid: 17.9 mg/L.
Test 4	Ozone concentration (aq): 6.1 mg/L; H_2O_2/O_3 mole ratio: 2/1; Pressure: ambient; Initial NAs concentration: Cyclohexaneacetic acid: 17.3 mg/L, Cyclohexanebutyric acid: 17.9 mg/L.
Test 5	Ozone concentration (aq): 6.1 mg/L; H_2O_2: not added; Pressure: ambient; Initial NAs concentration: Cyclohexaneacetic acid: 17.3 mg/L, Cyclohexanebutyric acid: 17.9 mg/L.
Test 6	Ozone concentration (aq): 6.1 mg/L; H_2O_2: not added; Pressure: 100 psi; Pressure cycles and time: 7 cycles in 10 min, 28 cycles in 40 min; Initial NAs concentration: Cyclohexaneacetic acid: 17.3 mg/L, Cyclohexanebutyric acid: 17.9 mg/L.

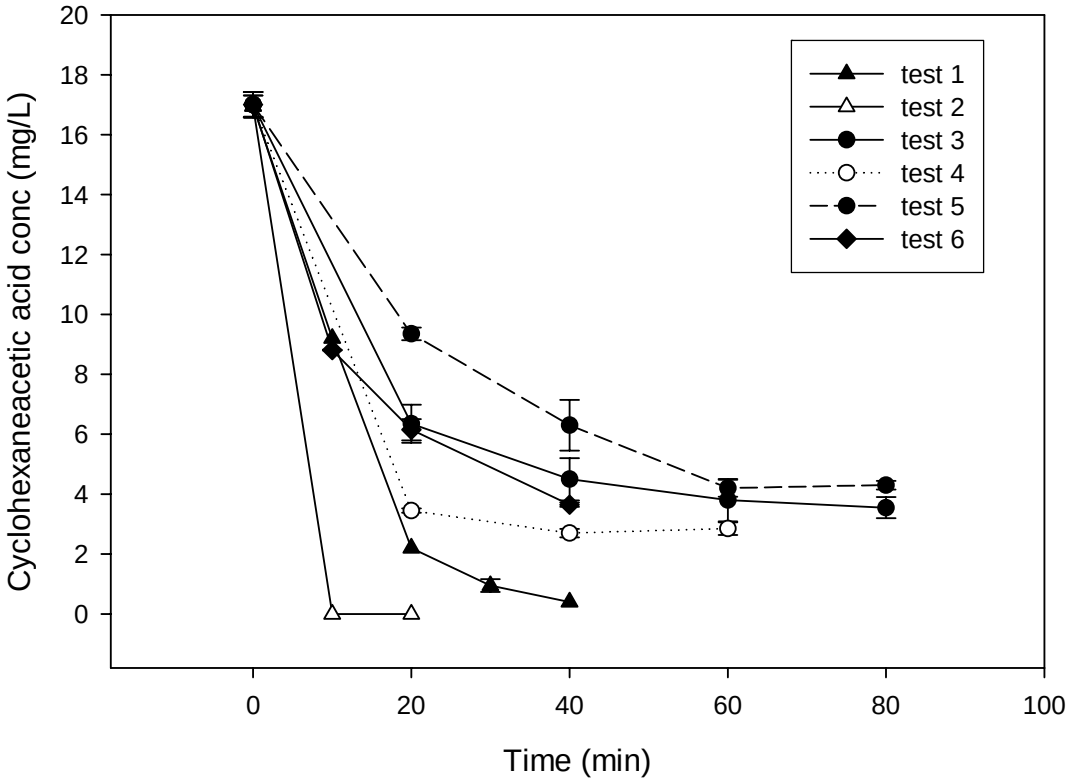


Figure 5.2. The removal of cyclohexaneacetic acid by ozone and hydrogen peroxide under different conditions

Oxidant dosages were the essential factors that affected the removal rate: when all the other experimental conditions (pressure of the system, reaction time, NAs initial concentrations) were the same, the higher the ozone concentration, the faster the target NAs were degraded. Furthermore, the addition of H_2O_2 into the system produced more OH radicals and triggered the indirect reaction between NAs and ozone, which also improved the removal efficiency.

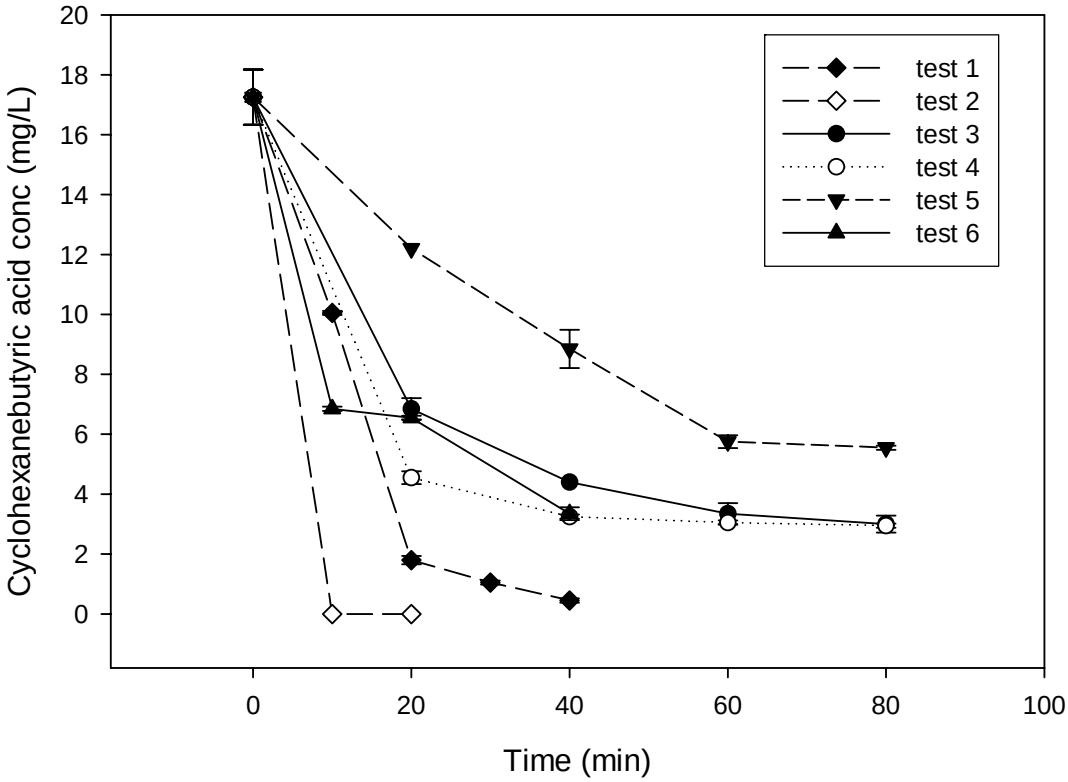


Figure 5.3. The removal of cyclohexanebutyric acid by ozone and hydrogen peroxide under different conditions

This strengthened the oxidation reaction and led to almost complete NAs removal. When the ozone concentration was 6.1 mg/L without H_2O_2, cyclohexaneacetic acid registered a removal percentage of 60.1% and cyclohexanebutyric acid registered 48.0% in 40 min. When the ozone concentration was increased to 14.8 mg/L, still without the addition of H_2O_2, the removal percentages of the 2 NAs increased to 97.6% and 96.9% respectively. Under this higher ozone concentration (14.8 mg/L) with the addition of H_2O_2, both NAs disappeared completely in only 10 min. The effect of H_2O_2/O_3 mole ratio on the removal of NAs was not as significant as O_3 dosage. A comparison of test 3 and test 4 results shows that when the H_2O_2/O_3 mole ratio was increased from 1/1 to 2/1, the 2

NAs were degraded about 15% faster in the beginning 40 min. After 60 min, the final NAs removal percentages under these two different H_2O_2/O_3 mole ratios would become close to each other. According to Equation 5.1, a H_2O_2/O_3 mole ratio of 1/2 was necessary for hydroxyl radical formation, when the water contained contaminants or other radical scavengers, the optimal ratio would be higher. Many researchers have found mole ratios between 0.5 and 1.4 brought about the fastest reaction rates [4].

$$2O_3 + H_2O_2 \rightarrow \bullet OH + 3O_2 \qquad (5.1)$$

PAO was more effective in treating the 2 target NAs. It increased the removal percentages of the 2 NAs by about 20% in the same reaction time of 40 min, because the microbubbles generated during compression-decompression cycles increased the ozone transfer efficiency, that target compounds, O_3 and ·OH congregated in a much higher concentration and reacted to each other more actively at the interfacial between gas phase and aqueous phase. The influence that these pressure cycles exerted on the degradation of NAs was almost as strong as the addition of H_2O_2, which could also promote the NAs removal percentage by approximately 20%. The degradation of NAs proceed rapidly during the beginning 20 min, it slowed down between 20 min and 40 min. The major portion of NAs removal took place within the first 40 min, after about 60 min the reaction nearly ceased under all the six experiment conditions. Level of pH became an important limiting factor when it was out of the optimal range for ozone chain reactions. In this research, pH value was less than 4 after 40 min of reaction time, under this pH levels, the generation of active free radicals was depressed, which was negative for the reaction between NAs and free radicals. It could be concluded that NAs were susceptible to both

the attack of O_3 and OH radicals, it showed degradability without the addition of H_2O_2 and their degradation would be increased by increasing pH or addition of H_2O_2.

According to Equation 5.2, the dissociate degree of NAs is [5]:

$$\alpha = 1 / (1+10^{pK-pH}) \qquad (5.2)$$

So at low pH levels the NAs were mostly present in their nondissociating form, which was less activating to O_3 attack. Thus the reactivity of NAs with ozone decreases with decreasing pH.

The NAs degradation by ozone might start from the oxidation of the carboxyl at the end of the branched chain, which would be attacked by ozone molecules or OH radicals and broken off to be oxidized to CO_2. The ozone molecules or OH radicals would continue to attack the rest of the alkyl chain through oxidation or nucleophilic reactions. This would happen first by the addition of oxygen atoms onto one or more of the carbon atoms, which would oxidize them into carboxyl. The carboxyl would then be turned into CO_2 and cut off from the alkyl chain, thus to break the alkyl chain or ring. This process occurred repeatedly to gradually cut the whole NAs molecule into short fragments, and finally come out with the terminal products of CO_2 and H_2O. Some NAs degradation products (product 3 to 8) were accumulated in the water solutions and were detected out by GC/MS. Take cyclohexanebutyric acid as example, the degradation pathway could be roughly described as shown in Figure 5.4.

5.5 Summary

In conclusion, both conventional ozonation and PAO were very effective in removing both of the two selected NAs in an aqueous environment, especially with high

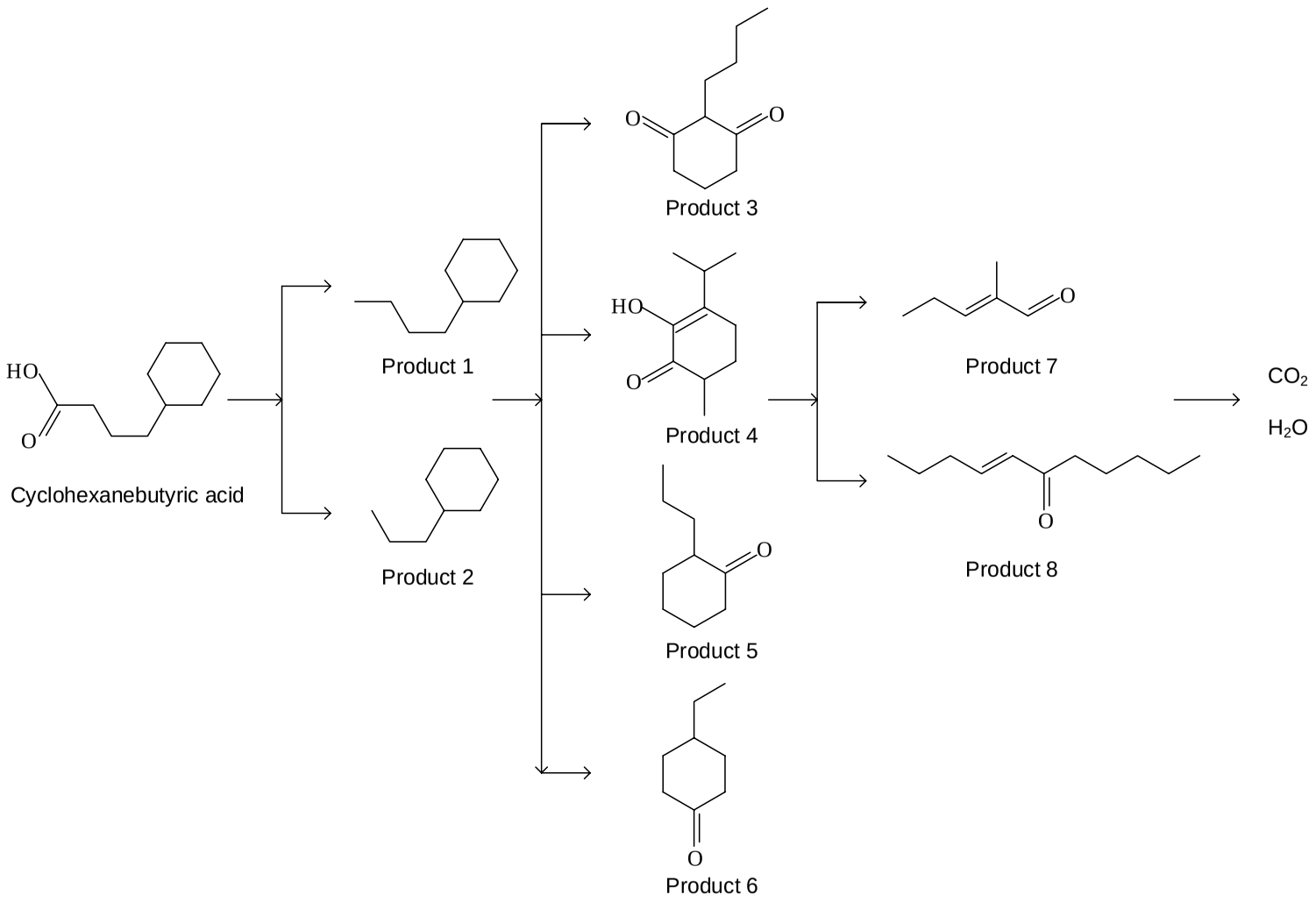


Figure 5.4. NAs degradation products and degradation pathway by ozonation

concentration of aqueous ozone and proper addition of H_2O_2, this helped greatly to degrade NAs more rapidly and completely. PAO could increase the removal percentage of the 2 NAs by approximately 20% during the same reaction times. This method could provide a feasible way for those sites that have oil spills or other pollution accidents that bring large quantity of NAs into the water to achieve quick local ecological remediation. Ozone could be produced onsite and the contaminants drawn into a reactor to be treated by PAO or by ozone and hydrogen peroxide under ambient pressure.

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CHAPTER 6

CONCLUSIONS

The new pressure-assisted ozonation (PAO) method using expanding O_3 microbubbles for degradation of Methyl *tertiary*-butyl ether (MTBE) is effective with a removal rate faster than previously achieved. MTBE degradation by 90% from an initial concentration of 12 mg/L was achieved in 36 minutes, which was 40% higher than under ambient pressure. Added H_2O_2 increased the treatment efficiency; however, the change of H_2O_2/O_3 mole ratios did not play an important role in the degradation kinetics of MTBE as long as H_2O_2 was present in the system. A 1/1 H_2O_2 to O_3 mole ratio was recommended. The compression-decompression cycles at 70 psi was enough to generate the microbubbles needed. Three MTBE degradation products were identified in this study including methyl acetate, isobutene, and acetone. The products tended to accumulate in the reaction solution initially and then gradually disappeared as degradation progressed.

Pressure-assisted ozonation treatment was more effective in removing EDCs and PPCPs compounds in water than ozonation treatment under ambient pressure conditions. Triclosan (TCS) and bisphenol A (BPA) were readily degraded by ozonation. They disappeared within minutes of PAO treatment at the initial concentration of around 9 mg/L respectively. PAO process increased removals of the four phthalate esters by about 15-25% higher than normal ozonation process within the same contact time of 24 min at

initial concentrations of 6.9~8.6 mg/L. The addition of H_2O_2 aided degradation but the effect was limited. Increasing compression cycles also favored the removal of target compounds, but the degradation nearly ceased after 60 cycles. Aqueous O_3 concentration was an important factor, with higher removal at higher O_3 concentration. Alkaline solution pH 7 and pH 10 were more favorable for the degradation of target compounds.

Degradation of MTBE and EDCs and PPCPs compounds was accelerated by the expanding microbubbles generated via successive compression-decompression cycles. The abundant interfacial region where contaminants are concentrated and where the reactive ozone has to migrate across to fill the expanding bubbles is attributed to as the cause of accelerated degradation.

For naphthenic acids (NAs), ozonation alone (at adequate concentration of 15 mg/L) was very effective in removing NAs in aqueous environment, although a small added amount of H_2O_2 (e.g., H_2O_2/O_3 mole ratio of 1/1) could enhance removal. Two NAs at initial concentration of 17 mg/L were degraded completely within 10 min. Pressure-assisted ozonation treatment increased the removal percentage of the 2 NAs by about 20% at the same contact time of 40 min, the effect was almost as intense as that of added H_2O_2 that increased the removal percentage of the two NAs by approximately 20%.

The results of this research on the ozonation of target waterborne contaminants suggested possible ozonation degradation of other organic compounds with similar chemical structure and properities.

CHAPTER 7

ENGINEERING APPLICATIONS OF PAO

The pressure-assisted ozonation (PAO) is a powerful technique in the removal of refractory organic compounds such as methyl *tertiary*-butyl ether (MTBE), phthalates, naphthenic acids (NAs) from various sources of contaminated waters.

For engineering applications, selecting a suitable reactor type for PAO operation is of great importance. These reactors include batch reactor, continuous flow reactor, fluidized bed reactor, fixed bed reactor etc. with different characteristics. In this research for the treatment of waterborne contaminants by PAO, batch reactors of different volumes are used, which are simple and easy to control. Usually batch reactors are more suitable for the treatment of small amount of contaminated samples, such as for the onsite treatment of contaminated sediment as shown in Figure 7.1. In this case, proper amount of sediment is transported by a slurry pump into the ozone reactor installed on a barge, treated by the PAO process, and then pumped back to the sediment layer.

However, continuous flow reactor is usually the preferred choice because of its continuous operation. For example, a continuous stirred-tank reactor (CSTR) takes influent continuously into the reactor at a certain flow rate, mixed completely for reaction, and then outputs the treated water from the reactor. The characteristic of CSTR is contrary to operation of the PAO process, because PAO must be closed to apply pressure.

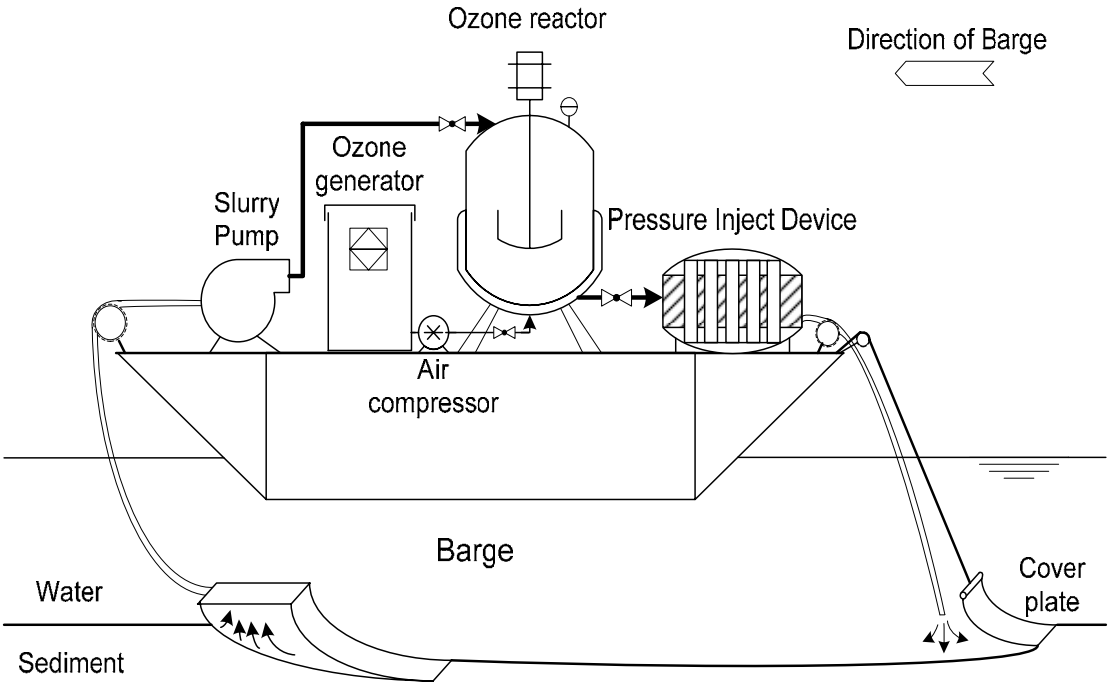

Figure 7.1. Onsite treatment of organics contaminated sediment by PAO process

This is a challenge for engineering applications of the PAO process.

Valves are helpful in resolving the conflicts between pressure cycles and continuous feeding, but the cost of the process might be increased for special design of the valves. A feasible way to solve this problem is to use several parallel batch reactors together to simulate the continuous flow reactor, which can be called pseudo continuous flow reactor as shown in Figure 7.2. In this reactor series, solenoid valves (1, 5, 9 and 2, 6, 10) are operated automatically by timer to control the supply of ozone/air mixture and gas venting. Valves (3, 7, 11 and 4, 8, 12) are used to control the influent and effluent of water. The operation of the PAO process can be divided into three stages: pumping in, reaction and pumping out. During the reaction stage, the reactor must be closed for the

purpose of applying pressure cycles. When reactor A is in the stage of intake, reactor B can be at the stage of PAO treatment and reactor C can be at the stage of discharge. The stages are subsequently rotated among the parallel reactors.

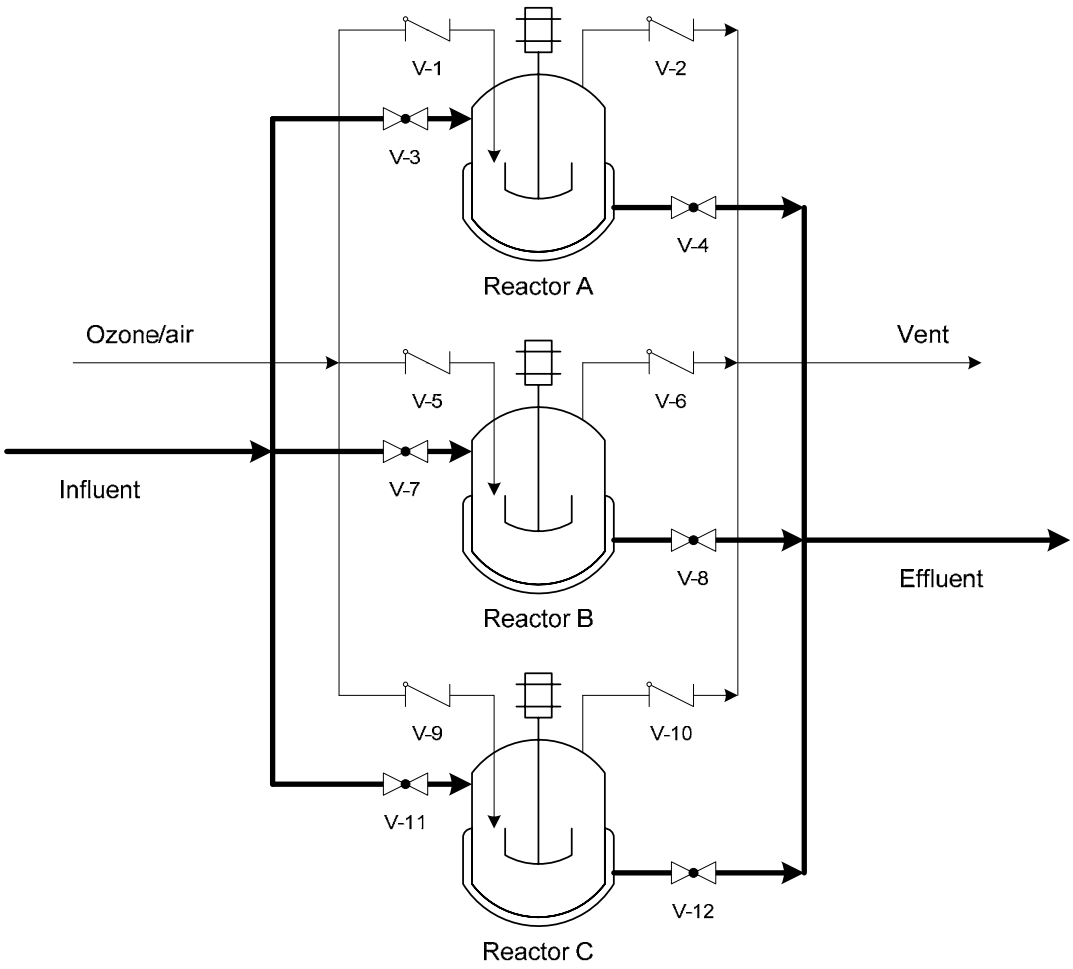

Figure 7.2. Pseudo continuous flow reactor for pressure assisted ozonation (PAO)